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Contributions from the New York Agricultural Experiment Station.

IV.—THE RELATION OF CARBON DIOXIDE TO PROTEOLYSIS IN THE RIPENING OF CHEDDAR CHEESE.

BY LUCIUS L. VAN SLYKE AND EDWIN B. HART.

In 1880 Babcock[1] carried on some experiments in cheese curing, in which he attempted to measure the amount of carbon dioxide formed by cheese in ripening, but his study of each cheese was limited to short periods of time and the source of the carbon dioxide formed was not ascertained by him. The investigation described in this paper was undertaken primarily to learn to what extent carbon dioxide is given off by American cheddar cheese during long periods of time in the process of ripening. It was hoped that by such study we should be able also to learn the sources of the carbon dioxide thus formed and add to our knowledge in regard to some of the deep-seated chemical changes occurring in the ripening of cheddar cheese.

As material for use in carrying on the investigation, we made two cheeses. One was normal in every respect; the other was made from milk containing chloroform and was kept under antiseptic conditions, thus enabling us to suppress factors of biological activity. The study was continued for thirty-two weeks, at the end of which time we completed the work by making a study of the end-products in each cheese, including, more particularly, diamido compounds and their secondary cleavage-products and tyrosine.

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[1] Cornell Univ. Expt. Sta. Rept., pp. 9–27 (1879–80).

EXPERIMENTAL PART.

Preparation of Cheese.

For each cheese we used about 20 kilograms of milk that had been drawn from the cows' udders not more than three hours. One cheese was made in the usual manner, being normal in every respect. In making the other cheese, we added to the milk at the start 4 per cent, by volume, of chloroform, and then enough lactic acid to equal 0.2 per cent of the milk by weight. The rest of the process of cheese-making was carried on in the usual way. In both cases salt was added at the rate of 1 part for 400 parts of milk used. The normal cheese weighed 3,000 grams. The cheese containing chloroform weighed 3,203 grams, owing to the retention of chloroform and more water.

Arrangements for Collecting Gas Evolved by Cheese.

On April 1, 1902, each cheese was placed by itself under a bell-jar, each bell-jar being connected with its own apparatus for the absorption of carbon dioxide. During the entire period of the investigation the cheeses were kept at a temperature of 15°.5 C. Through the bell-jars, made tight by mercury joints, were passed daily about 8 liters of air, previously purified by passage through several wash-bottles containing potassium hydroxide. The air from the bell-jar containing the normal cheese was passed through a drying-train of strong sulphuric acid and calcium chloride and then through two Liebig bulbs, in order to absorb any carbon dioxide present. A water-bottle holding 8.5 liters was used as an aspirator. The aspirator was started each morning at about eight o'clock and stopped at 5 P.M. Over night a stop-cock, separating the bell-jar from the wash-bottles containing potassium hydroxide and used for washing the inflowing air, was closed to prevent backward diffusion and consequent loss of carbon dioxide. The bulbs were weighed daily in the early period of the experiment, but only weekly during the later period.

In the case of the cheese containing chloroform, the air from the bell-jar was passed through sulphuric acid and then through silver nitrate solution, in order to absorb any hydrochloric acid formed by decomposition of chloroform. The air was then passed through three flasks containing a decinormal solution of barium hydroxide, to absorb the carbon dioxide, and finally through a potassium hydroxide guard. The same precaution against backward diffusion was observed as in the case of the other cheese. We could not employ Liebig absorption-bulbs and direct weighing, since the air coming from the bell-jar was constantly laden with vapor of chloroform. To replace the loss of chloroform caused by aspiration, fresh portions of chloroform were added, from time to time, through a separatory-funnel passing through the top of the bell-jar. A small dish placed on the top of the cheese received the chloroform. Once a week the barium carbonate formed was filtered through a weighed Gooch crucible, washed with dilute ammonia, dried, and weighed. From the amount of barium carbonate thus found the amount of carbon dioxide was calculated. On April 1st this cheese contained 12 per cent of chloroform, and on Nov. 28th, at the close of the investigation, 10.5 per cent.

The normal cheese, before being placed under the bell-jar, was completely covered on the outside by a mixture of vaseline and creosote, in order to prevent as far as possible the growth of any molds on the surface of the cheese. This was done at the suggestion of the Station bacteriologist, Mr. H. A. Harding. In a similar experiment, when no special precautions were used, Babcock[1] found it impossible to prevent the growth of molds on the surface of cheese contained in a moist atmosphere under a bell-jar. He calls attention to the fact that the growth of mold was responsible for the formation of large quantities of carbon dioxide. It was absolutely essential, therefore, that in our work we should eliminate this source of carbon dioxide, if we were to learn anything definite about other sources of carbon dioxide formation within the cheese.

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[1] Cornell Univ. Expt. Sta. Rept., p. 21 (1879–80).

Production of Carbon Dioxide in Normal Cheese.

On the first day we found the normal cheese had given off 0.044 gram of carbon dioxide, on the second day 0.0978 gram, on the third day 0.118 gram, and on the fourth day 0.139 gram. On the eleventh day, the maximum daily record up to that time was made, 0.146 gram. During the first week we found 0.735 gram of carbon dioxide, and this amount gradually decreased until the end of the fourth week, when the amount was 0.364 gram. At this time the bell-jar was opened and samples taken for chemical analysis. Before opening the bell-jar the aspiration was quickened somewhat in order to reduce the carbon dioxide in the bell-jar to the lowest amount possible. From the fourth to the ninth week the amount of carbon dioxide produced increased gradually, reaching 0.644 gram for the ninth week. At this time a small patch of blue mold, covering about a square inch of surface, was observed. This was scraped off and more creosote applied. At the end of the eleventh week another small patch of blue mold was noticed and the amount of carbon dioxide formed had again risen. Again, at the end of the thirteenth week, another small patch of mold was found, and the amount of carbon dioxide produced during this week was equal to that found during the first week of the experiment, 0.735 gram, the maximum weekly yield during the investigation. The whole outer surface of the cheese was then treated anew with the mixture of vaseline and creosote and afterwards no further trouble was experienced from the presence of molds. It was very noticeable that the presence of mold was quickly revealed by a sudden and marked increase in the amount of carbon dioxide formed. From the end of the thirteenth week to the close of the investigation, at the end of the thirty-second week, the amount of carbon dioxide gradually decreased, being only 0.224 gram during the last week.

During the entire period of thirty-two weeks the total amount of carbon dioxide produced was 15.099 grams. This is equal to 0.5 per cent of the fresh cheese and represents a loss of solids equal to one-half pound for 100 pounds of cheese. Undoubtedly other gases or volatile compounds are formed in small quantities, as shown by the blackening of the sulphuric acid in the drying-train. We hope to make later a more detailed study of the other gases formed in cheese during the ripening process. In the table following we present the detailed results of our work week by week :

Table I.—Amount of Carbon Dioxide Formed in Normal Cheddar Cheese during Each Week of Investigation.

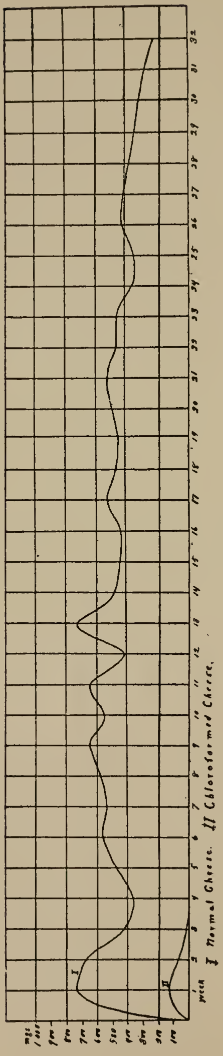
No. of week.	Gram of CO_2 formed.	No. of week.	Gram of CO_2 formed.	No. of week.	Gram of CO_2 formed.
1	0.735	12	0.406	23	0.462
2	0.672	13	0.735[1]	24	0.357
3	0.420	14	0.476	25	0.343
4	0.364	15	0.441	26	0.427
5	0.476	16	0.434	27	0.400
6	0.574	17	0.539	28	0.366
7	0.525	18	0.469	29	0.340
8	0.574	19	0.448	30	0.300
9	0.644[1]	20	0.497	31	0.260
10	0.539	21	0.539	32	0.224
11	0.651[1]	22	0.462		

Production of Carbon Dioxide in Cheese Containing Chloroform.

In the cheese containing chloroform we planned to suppress all biological activity. In order to ascertain how completely we succeeded in this respect, Mr. John Nicholson, the assistant bacteriologist of the Station, made bacteriological examinations from time to time. His results showed that the cheese was practically sterile throughout the entire period of the investigation.

The quantity of carbon dioxide produced by this cheese amounted only to about 0.019 gram a day during the first week, after which it fell off rapidly, the amount during the third week being less than 0.003 gram a day. At the end of three weeks carbon dioxide practically ceased to be formed. The total amount of carbon dioxide produced by this cheese was 0.205 gram, about three-fourths of which was given off during the first nine days.

[1] Increase due to presence of small amount of mold.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I
II
I Normal Cheese. II Chloroformed Cheese.

Fig. I.

In the accompanying diagram we show in graphic form the amounts of carbon dioxide produced by the two cheeses during the period of investigation.

Proteolytic End-Products in the Normal Cheese.

At the end of thirty-two weeks the normal cheese was taken from the bell-jar, the covering of vaseline and creosote was removed, and also the entire outer rind of the cheese to the thickness of about 0.5 inch. The remainder of the cheese was cut up into small pieces and dried at 60° C. for several days. It was then broken into finer particles and again dried, after which it was extracted with ether to remove fat and then reduced to a finely powdered, white mass. This mass was extracted with several portions of water at 50° C. until about 12 liters were collected, the water-soluble content of the mass having been thoroughly extracted by this treatment. This extract was precipitated with tannin and filtered; the tannin in the filtrate was removed by lead acetate. The resulting precipitate of lead tannate was filtered and washed three times by suspension in water and refiltering. The excess of lead was removed by sulphuric acid, and the last traces by hydrogen sulphide. The filtrate was then carefully concentrated at 55° C. to about 4 liters, made acid with 5 per cent of sulphuric acid, and precipitated with phosphotungstic acid. The precipitate was washed with dilute sulphuric acid. The filtrate from the phosphotungstic acid precipitate was examined for tyrosine and the precipitate for oxyphenylethylamine and the hexon bases.

Tyrosine.—The filtrate from the precipitate by phosphotungstic acid was treated with barium oxide to remove the phosphotungstic acid and the barium hydroxide in the filtrate carefully removed by sulphuric acid. This filtrate was concentrated to a small volume. On standing, crystals separated from the solution, having much the appearance of tyrosine. These were filtered, redissolved in water, recrystallized several times from water after concentrating the solution, finally washed with alcohol, and dried over sulphuric acid *in vacuo*. A nitrogen determination by the Kjeldahl process gave the following results:

	Calculated for $C_9H_{11}NO_3$.	Found.
Tyrosine	7.68	7.73

The substance gave the color reactions that are characteristic of tyrosine, and was undoubtedly tyrosine. The separation of other monamido compounds was not attempted.

Oxyphenylethylamine.—About one-fourth of the phosphotungstic acid precipitate, obtained in the manner previously described, was decomposed by barium oxide and filtered. The excess of barium hydroxide was removed from the filtrate by means of carbon dioxide. The clear filtrate was concentrated at a low temperature and then treated with benzoyl chloride in dilute alkaline solution, according to the Schotten-Baumann method.[1] This method has been employed by Langstein[2] in the separation of oxyphenylethylamine formed by an intense peptic digestion of egg-albumin. An abundant precipitate separated, which was filtered and washed with cold water. It was then dissolved in hot alcohol and evaporated to a small bulk. On standing, an abundant crop of crystals separated from the solution, which were filtered, washed with ether, and dried over sulphuric acid *in vacuo*. This product had a melting-point of 169° C. (uncorr.), agreeing exactly with the oxyphenylethylamine obtained by Langstein. The following results were obtained by determining the nitrogen by the Kjeldahl method and the carbon and hydrogen by combustion :

	Calculated for $C_8H_9NO(C_6H_5CO)_2$.	Found.
C	76.50	76.19
H	5.54	5.44
N	4.06	4.10

This product was unquestionably oxyphenylethylamine, formed, as we shall point out later, from tyrosine with the accompaniment of carbon dioxide as a by-product.

Hexon Bases.—The remainder of the phosphotungstic acid precipitate, obtained in the manner previously described, was decomposed by barium oxide and the excess of barium hydroxide was removed by careful addition of sulphuric acid. The resulting filtrate was worked for the hexon bases according to the Kossel-Kutscher method.[1]

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[1] Ber. d. chem. Ges., **17**, 2545 (1884) ; **19**, 3218 (1886).

[2] Beit. für chem. Physiol. u. Pathol., **2**, 229 (1902).

(1) *Arginine.*—After separating histidine from the solution, which should contain only arginine and histidine, a determination was made of the nitrogen in this solution containing only arginine. The amount of arginine thus determined, equivalent to the nitrogen found, was only 0.364 gram, an amount too small to obtain in the form of crystals.

(2) *Histidine.*—This substance was separated as the dichloride, of which we obtained 0.850 gram. Analysis gave the following results:

	Calculated for $C_6H_9N_3O_2.2HCl$.	Found.
N	18.42	18.15
Cl	31.11	30.98

(3) *Lysine.*—We separated about 2 grams of lysine in the form of picrate, which gave the following results on analysis:

	Calculated for $C_6H_{14}N_2O_2.C_6H_3N_3O_7$.	Found.
N	18.66	18.80
C	38.40	38.44
H	4.53	4.56

(4) *Guanidine.*—The mother-liquor from the lysine precipitate was extracted by a mixture of alcohol and ether and then treated with gold chloride in very dilute hydrochloric acid solution, following the method of Winterstein and Thöny.[2] On standing, there soon separated from the solution a crystalline substance, behaving like a guanidine gold salt, yielding about 0.300 gram, which, on analysis, gave the following results:

	Calculated for $CH_5N_3.HCl.AuCl_3$.	Found.
Au	49.79	49.63

So small an amount of this substance was obtained that we were unable to make other determinations to establish its identity with greater certainty, but it is highly probable that the substance is guanidine.

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[1] Ztschr. physiol. Chem., **31**, 165 (1900).

[2] *Ibid.*, **36**, 28 (1902).

(5) *Putrescine.*—We expected to separate the other cleavage-product of arginine, putrescine. The lysine solution had a strong odor of putrescine, and it was unquestionably present, but we failed in our efforts to isolate this base. It appears probable that the cleavage of arginine had only progressed as far as the formation of guanidine and ornithine, and that the latter compound had been decomposed only to a small extent, forming merely traces of putrescine. The fact that the cheese was of good flavor, except for a slight taste of creosote, indicates that putrescine could not have been present in considerable quantities.

Proteolytic End-Products in Cheese Containing Chloroform.

The cheese containing chloroform was, at the end of thirty-two weeks, treated, preparatory to extraction, in the manner described above in the case of the normal cheese. It was extracted with several portions of water at 50° C., until about 12 liters of extract were obtained, the mass having been completely extracted by this treatment. The water extract was treated with tannin and filtered, the tannin removed by lead acetate, and the precipitate filtered and well washed. The excess of lead was removed by sulphuric acid and the last trace by hydrogen sulphide. The filtrate was concentrated at a low temperature, never above 55° C., to a small volume. It was then precipitated by phosphotungstic acid, filtered, and well washed with dilute sulphuric acid.

Tyrosine.—After removing the phosphotungstic acid by barium oxide and then the barium hydroxide by careful treatment with sulphuric acid, the solution was concentrated to a small volume and set aside for crystallization. After standing several days, there separated from the solution a mixed crystalline and gummy mass. This precipitate was filtered, dissolved in a small volume of water, poured into cold 95 per cent alcohol, and allowed to stand several days. A crystalline precipitate formed at the bottom of the solution. The precipitate was filtered, redissolved in water, decolorized with charcoal, and filtered. On concentration, this filtrate deposited a copious crystalline precipitate, greatly resembling tyrosine in appearance. These crystals were washed with ether and dried over sulphuric acid *in vacuo.* A determination gave 7.70 per cent of nitrogen, as compared with 7.73, calculated for tyrosine.

We were unable to find in this cheese any trace of oxyphenylethylamine.

Hexon Bases.—The phosphotungstic acid precipitate was decomposed by barium oxide, the barium hydroxide was removed from the filtrate by sulphuric acid, and then arginine and histidine were precipitated by silver sulphate in barium hydrate solution in the usual way.

(1) *Arginine.*—After the separation of histidine from arginine, a determination of nitrogen in the remaining solution indicated the presence of about 1.5 grams of arginine, which is by far the largest amount we have ever succeeded in separating from any cheddar cheese with which we have worked. The solution was evaporated, dilute nitric acid added, and then set aside for crystallization. After standing about a week, the solution had partly crystallized. These crystals were removed by filtration, washed with absolute alcohol and ether, and dried over sulphuric acid *in vacuo.* Analysis gave the following results:

	Calculated for $C_6H_{14}N_4O_2.HNO_3.\frac{1}{2}H_2O$.	Found.
N	28.45	28.32

To the mother-liquor was added silver nitrate with 2 or 3 drops of dilute nitric acid, and the solution was allowed to evaporate *in vacuo.* Crystals soon separated, and after a few days the entire mass was crystalline. The crystals were washed with alcohol and ether and dried over sulphuric acid *in vacuo.* A silver determination gave the following results:

	Calculated for $C_6H_{14}N_4O_2.AgNO_3.HNO_3$.	Found.
Ag	26.54	26.49

We believe we are justified in regarding this substance as arginine, beyond question. So far as we are able to learn, this is the first time arginine has been separated from a ripening cheese, and, in this case, we succeeded only when all biological factors had been eliminated.

(2) *Histidine.*—This base was separated as a dichloride. Analysis gave the following results:

	Calculated for $C_6H_9N_3O_2.2HCl$.	Found.
Cl	31.11	31.08
N	18.42	18.59

(3) *Lysine.*—This substance was easily separated as the picrate, and analyzed as follows:

	Calculated for $C_6H_{14}N_2O_2.C_6H_3N_3O_7$.	Found.
N	18.69	18.78
H	4.53	4.38
C	38.40	38.51

We were unable to separate guanidine from the mother-liquor of the lysine precipitate, and we believe it was not present. We were unable, also to detect any of the other possible cleavage-products of arginine. The solution containing lysine had no such odor as the corresponding solution obtained from the normal cheese and was, indeed, conspicuously free from the putrescine odor that was so characteristic of the lysine solutions obtained from normal cheese ripened at about 15°.5 C.

Analysis of Cheese.

At intervals determinations were made of the moisture, total nitrogen, water-soluble nitrogen, and nitrogen in the form of unsaturated paracasein lactate, of amido compounds, and of ammonia. The results are given in the table on the following page.

If we compare the two cheeses in question with reference to the data contained in the table on page 13, we notice:

1. In respect to the water-soluble compounds of nitrogen, the two cheeses did not greatly differ, the slight difference being in favor of the chloroformed cheese. Ordinarily, we should expect the normal cheese to form soluble nitrogen compounds with somewhat greater rapidity than the cheese containing chloroform. Two conditions that were present

Table II.—Results of Analysis of Cheeses.

	Age when analyzed.	Per cent of moisture in cheese.	Per cent of nitrogen in cheese.	Nitrogen expressed as percentage of total nitrogen in cheese, in form of Water-soluble nitrogen.	Amido compounds.	Ammonia.	Paracasein monolactate.
Normal cheese	Fresh	36.53	3.54	6.78	2.52	0	58.47
	1 mo.	35.83	3.72	18.82	11.83	0.70	42.50
	3 mos.	34.84	3.92	25.50	17.86	1.78	33.42
	7 "	33.94	4.09	38.14	28.12	2.30	20.54
Cheese containing chloroform	Fresh	46.23	2.45	9.80	3.67	0	35.92
	1 mo.	45.77	2.50	20.80	11.20	0	22.40
	3 mos.	44.38	2.51	27.90	14.74	0	17.93
	8 "	44.37	2.73	40.30	23.10	0	7.33

furnish an explanation of these unexpected results. In the first place, some of the creosote used in coating the normal cheese diffused into the body of the cheese and exerted some antiseptic influence, retarding enzyme and bacterial action and giving proteolytic results lower than we commonly find in the case of normal cheese. In the second place, the chloroformed cheese contained about 10 per cent more water than the normal cheese. We have in our unpublished records numerous data which establish the fact that increase of moisture in cheese very noticeably increases the amount of water-soluble nitrogen compounds formed in a given time. At the last analysis, the chloroformed cheese was a month older than the normal cheese, and this fact also made greater the difference in the amount of water-soluble nitrogen compounds found in these analyses.

2. After the first month the amount of amido compounds formed in the normal cheese was greater than in the chloroformed cheese.

3. In the normal cheese ammonia was formed, though somewhat less in amount than under conditions entirely normal, while in the chloroformed cheese no trace of ammonia was formed.

4. We have previously[1] pointed out that the formation of water-soluble nitrogen compounds in cheese-ripening appears to take place at the expense of the paracasein monolactate (soluble in dilute solutions of sodium chloride). The figures in the preceding table furnish confirmatory evidence of this, since the paracasein monolactate diminishes at the same time the water-soluble nitrogen increases.

5. The amount of water-soluble proteolytic compounds formed in cheese cannot safely be used as the sole basis of comparison in respect to the extent of chemical changes taking place in ripening cheese. In the two cheeses investigated, the amounts of water-soluble nitrogen did not greatly differ, but an examination of the end-products of proteolysis showed changes much more complete in the case of the cheese containing the smaller amount of water-soluble nitrogen.

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[1] This JOURNAL, 28, 417 (1902).

The true measure of cheese ripening must be found in the character and amount of the individual products formed rather than in the total amount of water-soluble nitrogen.

General Summary of Results.

We now bring together, in a form allowing ready comparison, the results that have been presented in detail in the foregoing pages:

In Normal Cheese.	*In Chloroformed Cheese.*
(1) Production of carbon dioxide:	
a. Total in thirty-two weeks, 15.099 grams.	*a.* Total, 0.205 gram.
b. Weekly variation from 0.735 gram in first week to 0.224 gram in thirty-second week.	*b.* Ceased entirely after three weeks.
(2) Proteolytic end-products formed:	
a. Tyrosine in small am'ts.	*a.* Tyrosine.
b. Oxyphenylethylamine.	*b.* No oxyphenylethylamine.
c. Arginine in traces.	*c.* Arginine in marked quantity.
d. Histidine.	*d.* Histidine.
e. Lysine.	*e.* Lysine.
f. Guanidine.	*f.* No guanidine.
g. Traces of putrescine.	*g.* No putrescine.
(3) Analysis of cheese.	
a. Ammonia formed.	*a.* No ammonia formed.
b. Amido compounds more abundant.	*b.* Amido compounds less abundant.

DISCUSSION OF RESULTS.

We have seen above that results varying in a most marked manner were obtained from the two cheeses used in our investigation. We will now consider some of these differences with a view to finding some satisfactory explanation of the facts presented.

The Sources of Carbon Dioxide in Cheese.

What was the source of the carbon dioxide produced in each cheese? Why did the normal cheese produce relatively so large quantities of carbon dioxide over so long a period of time, and why did the chloroformed cheese produce so small quantities and for so brief a period?

As possible sources of carbon dioxide in cheese, we have (1) the milk used in making cheese, (2) the decomposition of milk-sugar in the formation of lactic acid, (3) the respiration of living cells present in the cheese, and (4) the chemical decomposition of compounds present in the cheese. We will consider these separately.

(*1*) *Milk as a Source of Carbon Dioxide in Cheese.*—According to Marshall,[1] fresh milk, before exposure to air, contains on an average about 4 per cent of free carbon dioxide by volume, and this is reduced one-half by aeration. In the amount of milk used by us in making each cheese, we should have about 0.800 gram of carbon dioxide. Some of this is, of necessity, lost in the process of cheese-making, but we could expect to retain in the cheese 0.200 to 0.300 gram of the carbon dioxide originally present in the milk.

(*2*) *The Decomposition of Milk-Sugar as a Source of Carbon Dioxide in Cheese.*—E. Kayser[2] has shown that certain lactic acid bacteria produce, as the result of their action on milk-sugar, not only lactic acid but also certain by-products, among which is carbon dioxide. The milk-sugar is undergoing decomposition all through the normal process of cheese-making, and the carbon dioxide thus formed becomes incorporated in the cheese curd to some extent. In our normal cheese, the milk-sugar actually present before the cheese was placed under the bell-jar amounted to 0.3 per cent of the cheese. This was changed into lactic acid with the accompanying formation of carbon dioxide in the early period of ripening, and the carbon dioxide thus formed, together with that occluded in the cheese mass, can readily account for the relatively large amount of carbon dioxide found during the first week in the normal cheese. In the case of the chloroformed cheese, a certain amount of the milk-sugar had undergone fermentation before chloroform was added, as shown by a determination of the sugar in the curd the day after the cheese was made. The amount found was low compared with the amount present in perfectly fresh curd. Such fermentation would produce small amounts of carbon dioxide, which would be absorbed by the milk and pass into the cheese mass. Carbon dioxide thus enclosed in a cheese would again be given out into an atmosphere such as was present in the bell-jar, that is, one free from carbon dioxide.

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[1] Special Bulletin No. 16, Mich. State Agr. Coll. Exp. Sta. (1902).

[2] Ann. Past., 8, 779 (1894).

(*3*) *Respiration of Living Cells Present in Cheese as a Source of Carbon Dioxide.*—It is well known that living cells give off carbon dioxide as the result of respiration processes. It is also known that in a fresh normal cheese of the cheddar type the number of micro-organisms, generally lactic acid bacteria, increases rapidly for about ten days, and then, after twenty-five days, falls very rapidly for a period of ten days to a relatively small number, as shown by Russell and Weinzirl.[1] In any case, we cannot look to the respiration processes of living cells in cheese as the source of the carbon dioxide formed after the first few weeks. As regards this possible source of carbon dioxide during the early age of a cheese, when the micro-organisms are present in enormous number, we should be justified in expecting that at this time the amount of carbon dioxide produced would be very much greater than that formed later, when the lactic acid organisms have largely disappeared, if their respiration is the source of any appreciable amount of carbon dioxide. The results secured by us with our normal cheese do not show that there was any such comparatively large amount of carbon dioxide produced at the time the lactic acid organisms were most abundant. The somewhat larger amount of carbon dioxide produced during the first two weeks is undoubtedly due mostly to the decomposition of milk-sugar and not to the respiration processes of living cells present in the cheese. In the case of our chloroformed cheese, we inhibited the activity of living organisms and this source of carbon dioxide did not, therefore, exist in the cheese.

[1] Ann. Rept. Wis. Expt. Sta., **13**, 95 (1896).

(4) *Chemical Decomposition of Compounds Present in the Cheese.*—Emerson[1] has lately shown that tyrosine, through the action of the enzymes of the pancreas, can be converted into the oxyphenylethylamine with simultaneous cleavage of carbon dioxide, in accordance with the following representation of the reaction :

$$HO.C_6H_4.CH_2.CH(NH_2).COOH = HO.C_6H_4.CH_2.CH_2.(NH_2) + CO_2.$$

Langstein[2] has also shown the same reaction in the case of a long-continued peptic digestion of the coagulated portion of the blood-serum of a horse. Ellinger[3] has shown the formation of putrescine from ornithine and of cadaverine from lysine, with the splitting-off of carbon dioxide, by the action of bacterial ferments. The following equations represent these reactions :

$$CH_2(NH_2).CH_2.CH_2.CH(NH_2).COOH = CH_2(NH_2).CH_2.CH_2.CH_2(NH_2) + CO_2;$$

$$CH_2(NH_2).(CH_2)_3.CH(NH_2).COOH = CH_2(NH_2).(CH_2)_3.CH_2(NH_2) + CO_2.$$

Lawrow[4] found the same reactions taking place in an intense peptic auto-digestion of the stomach.

The work of Nencki and of Spiro[5] has demonstrated that phenylethylamine can be formed from phenylalanine with separation of carbon dioxide.

Of these different reactions furnishing carbon dioxide, we find in the normal cheese under investigation evidence that tyrosine has changed into oxyphenylethylamine and that the decomposition of arginine has resulted in the formation of its simpler products. We cannot say whether Nencki's reaction occurred, by which phenylalanine was changed into phenylethylamine, since we did not examine the cheese for these compounds. It is readily conceivable that such a change may take place, since E. Fischer[6] has shown the presence of

[1] Beit. für chem. Physiol. u. Pathol., **1**, 501 (1902).

[2] *Ibid.*, **1**, 507 (1902).

[3] Ber. d. chem. Ges., **31**, 3183 (1898).

[4] Ztschr. phys. Chem., **33**, 312 (1901).

[5] Beit. für chem. Physiol. u. Pathol., **1**, 347 (1901).

[6] Ztschr. physiol. Chem., **33**, 151 (1901).

phenylalanine among the cleavage-products of casein. There probably await discovery other similar reactions, now unknown, bearing on the formation of carbon dioxide in proteolytic changes.

It appears to us that the carbon dioxide formed after the first few weeks of ripening, in the case of the normal cheese, must have come very largely from the decomposition of some compounds present in the cheese, among which we were able to identify the change of tyrosine and arginine into derived products with simultaneous formation of carbon dioxide. In the case of the different normal cheddar cheeses that we have previously investigated, the arginine and tyrosine commence to undergo proteolytic change quite early in the ripening process.

Reviewing briefly our discussion about the sources of carbon dioxide in cheese, we believe, from the evidence furnished, that the carbon dioxide given off in the early age of the normal cheese came largely from the decomposition of milk-sugar by lactic acid organisms, while a small amount was probably due to the carbon dioxide present in the milk and to the respiration of living organisms present in the cheese. The carbon dioxide produced after the first few weeks could apparently come only from the decomposition of some compounds present in the cheese, and we were able to identify among such sources of carbon dioxide the cleavage of tyrosine and of arginine.

In the case of the chloroformed cheese, none of the carbon dioxide could have come from the respiration of living cells or the decomposition of compounds like arginine and tyrosine. The amount of carbon dioxide originally present in the milk, combined with that formed in the milk from the decomposition of milk-sugar before treatment with chloroform, was sufficient to furnish the small amount that was given off by this cheese.

Cause of Difference in Behavior of Normal Cheese and Chloroformed Cheese.

We have seen that, in the chloroformed cheese, only an insignificant amount of carbon dioxide was present, and after three weeks practically none was found. In the normal cheese, carbon dioxide was found in relatively large quantities, and, even at the end of thirty-two weeks, more carbon dioxide was being formed in one week than the total amount produced in the other cheese. Why should there have been so marked a difference? The answer to this question involves a consideration of the causes that produce the proteolytic changes observed in the normal cheese-ripening process. The agencies sharing in this work are the following, so far as we know at present: (1) Some acid, (2) enzymes present in the milk before it is made into cheese, chief of which is galactase, (3) pepsin and pseudopepsin, added with rennet in the process of cheese-making, and (4) micro-organisms, chiefly bacteria.

In the case of our chloroformed cheese we had present, of these different agencies, acid, galactase, and rennet-pepsin. These agencies, under the conditions of our experiment, were unable to split carbon dioxide from tyrosine with the formation of oxyphenylethylamine, or change arginine into those of its products that we have commonly found in cheese ripening normally. As previously stated, this is the first instance in our knowledge in which arginine has been found in ripening cheese, and we were able to find it only because we had inhibited the action of living organisms. These facts suggest strongly that the active cause in our normal cheese that was responsible for the deep-seated proteolysis, accompanied by the production of carbon dioxide, was a biological factor.

It may be thought that our results fail to agree with those of Lawrow cited above, in which he succeeded by an autodigestion of a stomach in obtaining putrescine and cadaverine, probably with formation of carbon dioxide. It must be kept in mind, however, that in his work the conditions were favorable to a much more intense reaction, because he not only had a highly concentrated pepsin solution but he also kept the acid content of his digesting solution high, conditions that are not present in cheddar cheese.

It may be thought, again, that the activity of the enzymes, galactase and rennet-pepsin, was checked in our one cheese by the chloroform, and that we should, under the circumstances, expect just such results as we obtained. In Bulletin No. 203 of this Station, we have furnished evidence showing that chloroform does not inhibit the action of galactase, and we shall later publish results, secured in cooperation with the bacteriological department, confirming our previous work. Lawrow's work showed that chloroform did not inhibit the activity of a concentrated solution of pepsin. In view of the evidence at hand, it appears to us quite improbable that, if chloroform has any inhibiting influence on galactase and rennet-pepsin, we should find these two enzymes, under the conditions of the experiment, able to furnish such end-products as arginine, lysine, and tyrosine, but unable to produce compounds resulting from further proteolysis, such as putrescine, guanidine, and ammonia. If chloroform interfered with the work of these enzymes, we should expect either that there would be no proteolysis or that we should find the same compounds that are formed in the absence of chloroform but in much smaller quantities. As a matter of fact, we find these enzymes quite as active in the chloroformed cheese as in the normal cheese in forming certain compounds, but they stop short in their work, appearing unable to produce the further cleavage that results in the production of carbon dioxide. This failure to furnish products beyond a certain point seems to us to depend upon other conditions than the presence of chloroform.

The only logical conclusion suggested by the results of our work appears to us to be that the enzymes, galactase and rennet-pepsin, are able to furnish such end-products as arginine, lysine, and tyrosine under the conditions existing in cheddar cheese but are not able to split these compounds into simpler ones with simultaneous formation of carbon dioxide. If this is true, then we must look to some other source as the active agency in decomposing primary into secondary cleavage-products of proteolysis with production of carbon dioxide. The only cause that can be suggested is a biological factor.

Several investigators have made a study of the gases in cheese, especially in connection with the formation of holes in Emmenthaler cheese and the so-called "huffing" common to hard cheeses, and they have, without exception, attributed the formation of gases to micro-organisms. Thus, Baumann[1] found the gas in cheese examined by him to consist of 63 per cent of carbon dioxide. In this particular case he assigned *Bacillus diatryplicus casei* as the cause. Later von Klecki,[2] in a similar investigation, found gas produced in an inoculated milk containing 31.76 per cent of carbon dioxide and he attributed its formation to *Bacillus saccharobutyricus*. Adametz, Freudenreich, and Weigmann have assigned other organisms. Jensen[3] suggests that the gas that causes holes in cheese is mostly carbon dioxide, and that this comes from the action of lactic acid bacteria upon the nitrogen compounds of the cheese. While no one, probably, has yet solved the problem as to what specific organism or organisms are responsible for the deep-seated chemical changes occurring in cheese, the general tendency has been to look to some biological source as a prominent factor in cheese-ripening.

From the consideration of quite different data, we previously[4] arrived at the conclusion that there is a biological factor at work in normal cheese-ripening. In the results presented in this paper and also in the case of a large number of results not yet published, we always find that in a chloroformed cheese, where galactase and rennet-pepsin are the only proteolytic agents present, we never have ammonia formed, while we always find it early in normal cheese. In these cases the only difference appears to be the presence or absence of a biological agent.

What specific organism or combination of organisms may constitute this biological factor in cheese-ripening, we are not now able to say. In cooperation with the bacteriological department of this Station, we have work in progress by which we hope definitely to establish whether those deep-seated chemical changes in cheese-ripening, which cannot be attributed to galactase or rennet-pepsin, are due to lactic acid organisms or to liquefying bacteria and their enzymes, or to some combination of these.

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[1] Landw. Versuchssta., 42, 181 (1892).

[2] Centrbl. f. Bakteriol. u. Parasitenk., 2, 21 (1896).

[3] *Ibid.*, 4, 217 (1898).

[4] Bull. No. 203, N. Y. Agr. Expt. Sta., p. 244 (1901).

Summary.

1. The object of the work described in this paper was to ascertain the extent to which carbon dioxide is formed in American cheddar cheese during long periods of time in the process of ripening, and also to learn the nature of the chemical changes that give rise to the production of this gas.

2. Two cheeses were used for this study. One was entirely normal, the other was made from milk containing chloroform and kept under antiseptic conditions. The investigation was continued thirty-two weeks, when a chemical study was made of the proteolytic end-products.

3. In the normal cheese, carbon dioxide was given off continuously, though in decreasing quantities after about twenty weeks, and had not ceased at the end of thirty-two weeks. The total amount thus produced was 15.099 grams, equal to 0.5 per cent of the fresh cheese. In the chloroformed cheese, the total amount of carbon dioxide produced was 0.205 gram, practically none being found after three weeks.

4. In the normal cheese the following end-products of proteolysis were found: Tyrosine, oxyphenylethylamine, arginine in traces, histidine, lysine, guanidine, putrescine in traces, and ammonia. In the chloroformed cheese were found the same compounds, excepting oxyphenylethylamine, guanidine, putrescine, and ammonia, but arginine was found in marked quantities for the first time in cheese.

5. A consideration of the possible sources of carbon dioxide in the two cheeses indicates that, in the case of the chloroformed cheese, the carbon dioxide came from that present originally in the milk and that formed in the milk from the decomposition of milk-sugar before treatment with chloroform. In the case of the normal cheese, the carbon dioxide given off in its early age came largely from the decomposition of milk-sugar by lactic acid organisms, while a small amount was probably due to the carbon dioxide present in the milk and to

the respiration of living organisms present in the cheese. The carbon dioxide produced after the first few weeks came apparently from reactions taking place in some of the amido compounds, among which we were able to identify the change of tyrosine and arginine into derived products with simultaneous formation of carbon dioxide. Deep-seated proteolysis can take place without formation of carbon dioxide, but not apparently beyond a certain line of cleavage.

6. In the chloroformed cheese, the only active proteolytic agents were lactic acid, galactase, and rennet-pepsin. Under the conditions of our experiments, these agents were able to form neither ammonia nor secondary amido compounds with production of carbon dioxide. The presence of chloroform could not account for this lack of action. These results suggest that, in the normal cheese, there must have been some agent at work not present in the chloroformed cheese, and that this extra factor was of a biological character.

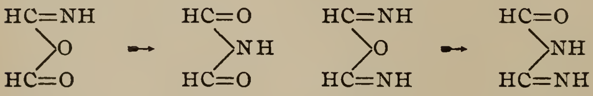
GENEVA, N. Y., February 15, 1903.

Contributions from the Sheffield Laboratory of Yale University.

CV.—ON THE MOLECULAR REARRANGEMENT OF IMIDOACID ANHYDRIDES.

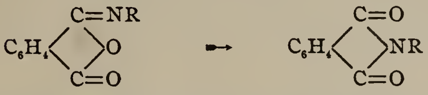
BY HENRY L. WHEELER AND TREAT B. JOHNSON.

The work described in this paper was undertaken with the object of investigating the formation and properties of some imidoacid anhydrides, compounds which may be considered as substitution-products of the hypothetical monoimidoformic anhydride (I.). Derivatives of this type would be expected to undergo a molecular rearrangement into diacylamides (II.), and in the same manner substitution-products of diimidoformic anhydride (III.) should be transformed into acylamidines (IV.):

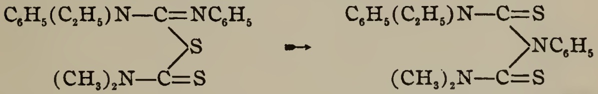


I. II. III. IV.

This property could be predicted from the fact that Hoogewerff and Van Dorp[1] and others[2] have observed this metastatic change to take place among cyclo-compounds. For example, the isophthalimides, on heating, give phthalimides:



It could be looked for, not only on account of the similarity in structure between such imido acid anhydrides and the imido esters, but also since Billeter[3] has shown that this rearrangement takes place in the case of acycloimidothiocarbamic anhydrides. He states that α-dimethylethyldiphenylpseudodithiobiuret (V.), at 100°, is transformed smoothly into dimethylethyldiphenyldithiobiuret (VI.):



V. VI.

Werner[4] found by the action of benzhydroximic chloride on silver benzoate that dibenzhydroximic acid (VII.) resulted. This oximidoacid anhydride was observed to undergo a molecular rearrangement at ordinary temperatures, giving dibenzhydroxamic acid (VIII.). In this case the benzoyl group migrates from one oxygen atom to another:

$$\underset{\text{VII.}}{C_6H_5C(O.COC_6H_5)=NOH} \rightarrow \underset{\text{VIII.}}{C_6H_5C(OH)=NO.COC_6H_5}.$$

It would seem probable that, like the above, the action of anilideimide chlorides on silver salts would give imidoacid anhydrides. We therefore caused benzanilideimide chloride, in ether and in the cold, to act on dry silver acetate with the hope of obtaining the following reaction:

$$C_6H_5C(Cl)=NC_6H_5 + AgOCOCH_3 = \\ C_6H_5C(OCOCH_3)=NC_6H_5 + AgCl.$$

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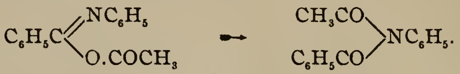
[1] Rec. trav. chim. Pays-Bas, **12**, 12; **13**, 93.

[2] Van der Meulen: *Ibid.*, **15**, 282.

[3] Ber. d. chem. Ges., **26**, 1688 (1893).

[4] *Ibid.*, **27**, 2198 (1894).

The product, however, did not have the above constitution. It proved to be identical with the diacylanilide prepared from mercury acetanilide[1] and benzoyl chloride. It therefore has both acyl groups attached to nitrogen, and its structure is to be represented by formula IX., the following molecular rearrangement having taken place in the cold :



IX.

When benzanilideimide chloride is allowed to act in the cold on silver parabrombenzoate a well-crystallized, stable substance is formed which, on boiling with alkali, gives a mixture of the two anilides and the two acids. To determine the structure of this substance, we allowed the imide chloride of the anilide of parabrombenzoic acid to act on silver benzoate, whereupon, instead of obtaining a different substance, it was found that the products were identical. It follows that the imidoacid anhydrides first formed in these reactions undergo a molecular rearrangement in the cold, as shown by the arrows :

$$C_6H_5C(OCOC_6H_4Br){=}NC_6H_5 \rightarrow$$
$$C_6H_5CON(C_6H_5)COC_6H_4Br \leftarrow$$
$$BrC_6H_4C(OCOC_6H_5){=}NC_6H_5.$$

As the above imidoacid anhydrides proved to be so unstable we next tried a different type of imide chloride, namely, ethylanilidochlorformate.[2] This, with silver benzoate, also gave a stable substance which, when treated with alkali, separated the benzoyl group. Since the N-diacylanilides that have been described in previous articles decompose with the liberation of the lower acyl group, it would appear that here we had to deal with a stable imidoacid anhydride. On the other hand, this conclusion was shown to be incorrect by the fact that the same substance results on treating phenylbenzimidoethyl ester with chlorcarbonic ester, a reaction involving addition which invariably gives N-derivatives.[3]

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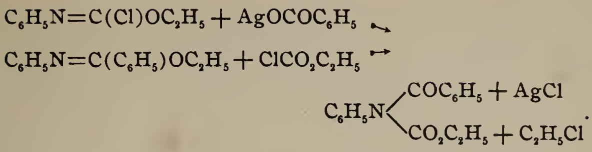
[1] Wheeler and McFarland: This JOURNAL, **18**, 546 (1896).

[2] Lengfeld and Stieglitz : *Ibid.*, **16**, 73.

[3] Wheeler and Walden : *Ibid.*, **19**, 130 ; **20**, 64.

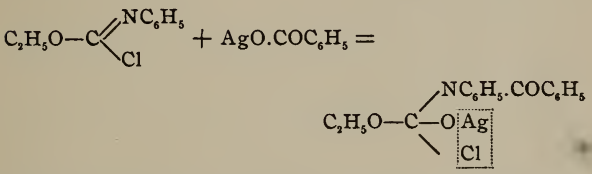


$$C_6H_5N{=}C(Cl)OC_2H_5 + AgOCOC_6H_5 \searrow$$

$$C_6H_5N{=}C(C_6H_5)OC_2H_5 + ClCO_2C_2H_5 \nearrow$$

$$C_6H_5N\begin{cases} COC_6H_5 + AgCl \\ CO_2C_2H_5 + C_2H_5Cl \end{cases}.$$

This reaction of acid chloride on the imidoester suggested that perhaps the mechanism of the action of silver salts on imide chlorides is analogous,—that the formation of N-diacylanilides does not involve a molecular rearrangement but takes place by addition. A separation of silver chloride, as indicated by the dotted lines in the following would then give the diacylanilide:

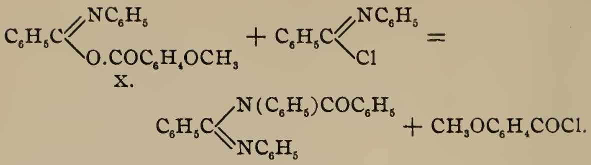


$$C_2H_5O{-}C\begin{cases} {=}NC_6H_5 \\ Cl \end{cases} + AgO.COC_6H_5 =$$

$$C_2H_5O{-}C\begin{cases} NC_6H_5.COC_6H_5 \\ {-}O\boxed{Ag} \\ \boxed{Cl} \end{cases}$$

That this is not the case and that imidoacid anhydrides are formed is shown by experiments with benzanilideimide chloride and silver anisate. In this case we isolated three products, the N-diacylanilide, anisic anhydride, and a compound which by a separate synthesis was identified as benzoylbenzenyldiphenylamidine. The formation of this amidine derivative and the anisic anhydride involve the previous formation of phenylimidobenzoicanisic anhydride (X.) below. Two molecules of this mixed anhydride might then decompose into anisic anhydride and a diimido anhydride, a derivative of formula III. above. This, by molecular rearrangement, would be expected to give the acylamidine.

It seems more probable, however, that the imidoacid anhydride first formed partially undergoes a molecular rearrangement, while the remainder acts with the anilideimide chloride, separating anisyl chloride and forming the amidine:



$$C_6H_5C\Big<\begin{array}{l}NC_6H_5\\ O.COC_6H_4OCH_3\end{array} + C_6H_5C\Big<\begin{array}{l}NC_6H_5\\ Cl\end{array} = C_6H_5C\Big<\begin{array}{l}N(C_6H_5)COC_6H_5\\ NC_6H_5\end{array} + CH_3OC_6H_4COCl.$$

X.

The anisyl chloride thus formed acts on a portion of the silver anisate, yielding anisic anhydride. This explanation is the more probable since Lander[1] found that benzoylbenzenyldimethylamidine results as a by-product in the action of benzmethylimide chloride on sodium ethylate, that is to say, the imide chloride acts on the imidoester first formed in the same manner as above.[2]

The results now at hand afford a satisfactory explanation for the behavior of the sodium and silver salts of amides and anilides with acid anhydrides[3] and acyl chlorides.[4] Salts of the type $C_6H_5C(NH)OAg$ give nitril and acid with acyl chlorides, while the N-substituted salts $HC(NC_6H_5)OAg$ give diacylanilides. In both cases imidoacyl anhydrides are formed as the first step of the reaction. Instead of the chloride acting by addition, as previously supposed,[5] the acyl group directly replaces the metal. The products in the former case decompose at ordinary temperatures, while those in the latter rearrange into N-derivatives. The action is similar to that of alkyl halides, but the imidoacid anhydrides undergo a molecular rearrangement with far greater ease than the imidoesters.[6]

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[1] Proc. Chem. Soc. (London), 19, 15 (1903).

[2] Lander (J. Chem. Soc., 81, 592 (1902)) also found that benzoylbenzenyldiphenylamidine results when benzanilideimide chloride and sodium ethylate react. The reaction is simply that of an acid chloride on an imido ester (see Wheeler and Walden: *Loc. cit.*).

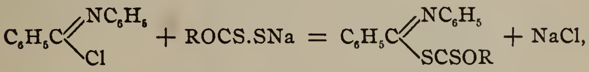
[3] Blacher: Ber. d. chem. Ges., 28, 435.

[4] Wheeler and Boltwood: This JOURNAL, 18, 381 (1896).

[5] Wheeler: *Ibid.*, 18, 695 (1896).

[6] In regard to the molecular rearrangement of imidoesters in general, by heating with alkyl halides, the curious fact has been observed by Mr. Henry F. Merriam that the aliphatic imidoesters do not undergo this transformation under the same conditions as those found to be successful in the case of the aromatic compounds (This JOURNAL, 21, 185; 23, 135). For example, acetimidomethyl ester was heated with methyl iodide at various temperatures from 100° to 135°, but little, if any, molecular rearrangement took place.

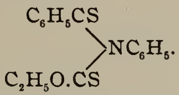
The so-called new class of colored organic compounds, or imidoxanthides, which Tschugaeff[1] has prepared from benzanilideimide chloride and certain xanthogenic salts, and which are represented as being formed as follows:



$$C_6H_5C\left\langle\begin{matrix}NC_6H_5\\ Cl\end{matrix}\right. + ROCS.SNa = C_6H_5C\left\langle\begin{matrix}NC_6H_5\\ SCSOR\end{matrix}\right. + NaCl,$$

are probably not imido anhydrides at all but rather dithiodiacylanilides, both groups being attached to nitrogen. Thiodiacylamides, in general, are colored.

Mr. George S. Jamieson has found that the bright-red product described by Tschugaeff from benzanilideimide chloride and potassium xanthate is a stable substance. On melting it forms a varnish which, when recrystallized, gives the unaltered material melting at the same temperature. It therefore probably has the structure



$$\left.\begin{matrix}C_6H_5CS\\ C_2H_5O.CS\end{matrix}\right\rangle NC_6H_5.$$

In regard to cycloimidoacid anhydrides, it may be stated that there are three classes:

(*a*) The isoimides of Hoogewerff and van Dorp, which may be viewed as derived from the prototype, formula I., by replacing the two hydrogen atoms of the HC groups by a bivalent radical. They contain the imido group outside the ring.

(*b*) Those which are derived by replacing the hydrogen attached to nitrogen and that of the adjacent HC group, forming a ring structure. In this case an acyl group is outside of the ring, and

(*c*) Where the hydrogen attached to nitrogen and that of the more remote HC group are replaced. This class contains the entire imidoacid anhydride structure within the ring. For example, the as yet unknown oxygen anhydride of acetylanthranilic acid, XI., which should give the acetylanthranil, XII., described by Bredt and Hof,[2] belongs to this class.

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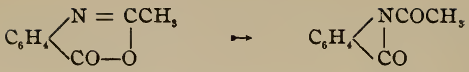
[1] Ber. d. chem. Ges., **35**, 2470 (1902).

[2] *Ibid.*, **33**, 29 (1900).



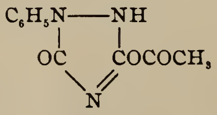
XI. XII.

Apparently no representatives of class *c*, ketometaoxazines or β-ketooxazolines, have been prepared. A number of cycloimidoacid anhydrides of the other class (*b*), however, are to be found in the literature.

Whether many of these compounds are actually imido anhydrides or acid amides is still an open question,[1] and, as far as the authors are aware, no member of this type of imidoacid anhydrides has been shown to undergo a molecular rearrangement.[2]

In view of the ease with which the above imidoacid anhydrides undergo a metastatic change, it seemed that this property should be met with in this series and perhaps could be used as a reliable means of distinguishing between a nitrogen and an oxygen derivative.

We selected for examination an acetyl derivative of phenylurazole. Acree[3] states that "when the silver salt of phenylurazole is treated with acetyl chloride in benzene solution in the cold, a reaction slowly takes place and the odor of acetyl chloride disappears. From the benzene solution there is obtained an oil having the constitution" XIII. (1-phenyl-3-acetylurazole):



XIII.

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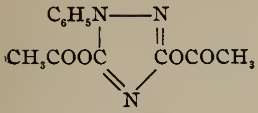
[1] Acree has discussed the possibility of determining their structure by examining the ease with which they are saponified by boiling with alcohol and water. An anhydride should be readily hydrolyzed by boiling water. This, in some cases, may serve as an indication of an anhydride structure, but unfortunately for this test certain acylamides also liberate an acyl group by this treatment, diacetanilide for example, and it is reasonable to assume that beside acetylphthalimide many other cyclotriacylamides will be found to do the same. See Rupe and Labhardt: Ber. d. chem. Ges., **36**, 1104 (1903).

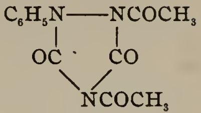
[2] A sulphur derivative of this type, *viz.*, the monobenzoyl derivative of methylaminothiopyrimidine, has been shown by Gabriel and Colman (Ber. d. chem. Ges., **32**, 2927 (1899)) to be transformed into a stable, higher melting isomer on heating.

[3] This JOURNAL, **27**, 118 (1902); Ber. d. chem. Ges., **35**, 553 (1902).



M. P. 115°.

XIV.



M. P. 162°.

XV.

When we undertook to perform this experiment we found that our results departed widely from those of Acree's. On evaporating the benzene spontaneously we obtained a beautifully crystallized mass of material and no oil. The product agreed with Acree's only in one respect—on boiling with water it reverted to phenylurazole. It therefore had the property which Acree assigns to an imidoacid anhydride. In fact, on heating to about 115° it melted, then solidified in the hot bath, and did not melt again until about 162°. The latter melting-point is that assigned by Thiele and Schleussner[1] to their diacetylphenylurazole which, on boiling with water, separates one acetyl group, giving a monoacetyl derivative melting at 170°. We found that our material, after heating, behaved in this manner and the compounds were identical. This behavior and the analytical results show that the labile compound first formed, melting at 115°, is a diacetyl and not a monoacetyl derivative. It is an imidoacid anhydride which changes into an amide derivative on heating, and the same molecular rearrangement, therefore, occurs in this series as in those previously considered.

In regard to the structure of these products, it is probable that in the case of Thiele's monoacetyl derivative, not saponified by water, the acetyl group is at 2, the most basic position.

Since the labile compound, melting at 115°, gives up both acetyl groups on boiling with water, one cannot be at position 2. This leaves a choice of positions 3 and 4, 3 and 5, or 4 and 5, the latter being the least probable of all, while from the behavior of ethyl iodide with the silver salt described below the positions 3 to 5 are most probable (formula XIV.). The diacetylurazole melting at 162° is best represented by the amide structure shown by formula XV. (1-phenyl-2,4-diacetylurazole) ; the molecular rearrangement therefore involves a double change as shown by the arrow.

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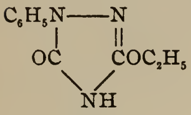
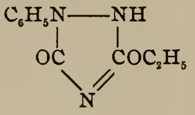
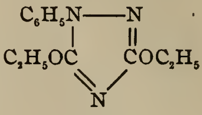
[1] Ann. Chem. (Liebig), 295, 171.

Several years ago Dr. Bayard Barnes and the writer[1] prepared an ethoxyphenylurazole, soluble in alkali, from carbethoxythionurethane and phenylhydrazine. To this substance we assigned the structure represented by formula XVI.[2]


XVI.


XVII.


XVIII.

In his paper on the constitution of phenylurazole Acree states that by treating the silver salt of the urazole with ethyl iodide an isomeric ethoxyphenylurazole was obtained. He states that this isomer is insoluble in alkali, and, therefore, he assigns the structure XVII. to the compound.

It seemed incredible that a monoethyl derivative of phenylurazole should be insoluble in alkali. It is the usual experience[3] that two such tautomeric formulas as XVI. and XVII. represent a single chemical individual and not two distinct substances. In our work[4] on the amidines, we encountered no case of isomerism like this.

We therefore treated the silver salt of phenylurazole with ethyl iodide in the cold, according to directions, and obtained an oil which gradually solidified, as stated by Acree. This product was a mixture of regenerated phenylurazole and a compound insoluble in alkali. The insoluble material had all of the properties which Acree assigns to the compound, except that it melted at 46° to 47° instead of at about 141°. Our analytical results showed conclusively that this material is not a mono-, but a diethyl derivative, and the insolubility is therefore explained. Formula XVIII. represents the structure of the compound, since on boiling with hydrochloric acid it readily gives off the ethyl groups and is converted into phenylurazole. There is, therefore, no reason to select any other than the usual one of the five tautomeric forms of phenylurazole as especially representing its structure.[1]

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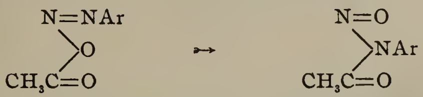
[1] J. Am. Chem. Soc., **22**, 368 (1900).

[2] It has not been proved that this substance has not the isomeric structure, 1-phenyl-5-ethoxyurazole. The rule which has been observed in the action of phenylhydrazine on thionurethanes (This JOURNAL, **27**, 259 (1900)), would suggest, however, that formula XVI. is correct.

[3] Marckwald: Ann. Chem. (Liebig), **286**, 356 (1895) ; Pechmann: Ber. d. chem. Ges., **28**, 869, 2362 (1895) ; Dimroth : *Ibid.*, **35**, 1038 (1902) ; Ley and Holzweissig : *Ibid.*, **36**, 18 (1903).

[4] This JOURNAL, **19**, 367 (1897) ; *Ibid.*, **20**, 853 (1898) ; Ber. d. chem. Ges., **32**, 35 (1899).

It is interesting to note in connection with the above molecular rearrangements that the formation of nitrosoacid anilides from *syn-* and *anti*-diazo acetates[2] involves a metastatic change similar to that observed by us. The analogy is shown on comparing formulas I. and II. with the following :



The molecular rearrangement of O-acetylacetoacetic ester[3] to the C-isomer is also comparable to that which we describe.

The results of our work, so far, indicate that when an acyl derivative, stable on heating, is obtained from a compound having the structure $-\mathrm{CONH}-$ or $-\mathrm{C(OH)=N}-$ the acyl radical is attached to nitrogen.

EXPERIMENTAL PART.

Benzanilideimide Chloride and Silver p-Brombenzoate.—Eight grams of the former and 14 grams of the latter were suspended in 110 cc. of dry ether and allowed to stand at ordinary temperature. At the end of twelve hours the imide chloride had completely reacted with the silver salt and a beautiful mass of colorless prisms had separated from the ethereal solution. The material melted at 149° to 150°, without purification, and when crystallized from alcohol it melted constantly at 150°. A nitrogen determination gave :

	Calculated for $C_{20}H_{14}O_2NBr$.	Found.
N	3.68	3.37

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[1] Compare Busch : Ber. d. chem. Ges., **35**, 1562 (1902). Knorr : *Ibid.*, **28**, 708 (1895).

[2] Hantzsch and Wechsler : Ann. Chem. (Liebig), **325**, 229 (1902).

[3] Claisen and Haase : Ber. d. chem. Ges., **33**, 3778 (1900) ; Wislicenus and Körber : *Ibid.*, **34**, 218 (1901).

p-Brombenzanilideimide Chloride, $BrC_6H_4C(Cl)=NC_6H_5$.—Parabrombenzoic anilide (15.3 grams) and phosphorus pentachloride (13.5 grams) were heated to 150° to 160° and the phosphorus oxychloride distilled off as far as possible at this temperature. On cooling, a mass of long needles separated which, on washing with ligroin, melted at about 78°. This imide chloride was found to be very sensitive towards moisture. On attempting to crystallize the material from ligroin it reverted to the anilide. The material for use was distilled at 12 mm. pressure, whereupon it practically all boiled at 200° to 210°, mostly at 205° to 207°. A portion of this, which melted at 78°, was analyzed with the following result:

	Calculated for $C_{13}H_9NClBr$.	Found.
N	4.75	4.87

This imide chloride is easily soluble in benzene and ligroin.

p-Brombenzanilideimide Chloride and Silver Benzoate.—The freshly distilled imide chloride (5.7 grams) was dissolved in dry benzene and the silver benzoate (6 grams) added. In this case the mixture was warmed for about one hour on the steam-bath. After filtering and cooling, the benzene deposited minute crystals which, when crystallized from alcohol, formed beautiful long needles or prisms. These melted at 150° and when they were mixed with some of the material prepared in the opposite way the melting-point was not lowered. A nitrogen determination gave:

	Calculated for $C_{20}H_{14}O_2NBr$.	Found.
N	3.68	3.83

p-Brombenzoylbenzanilide, obtained by these methods, is readily soluble in hot alcohol, but difficultly in cold, and more easily in benzene. When warmed with alkali, in alcoholic solution, it gives a mixture of parabrombenzanilide, benzanilide, benzoic, and parabrombenzoic acids.

Benzanilideimide chloride and silver acetate reacted slowly in cold ether. At the end of twelve hours the reaction was complete. On evaporating the ethereal solution in a vacuum the crude crystalline residue, washed with water, melted at about

62° to 63°. On crystallizing from dilute alcohol it melted at 68° and proved to be identical with acetbenzanilide previously described.[1]

Ethyl Phenylimidochlorformate and Silver Benzoate.—Five grams of the ester and 7 grams of the salt were mixed in dry ether and allowed to stand. At the end of twelve hours the ether still contained a large amount of chloride, and a strong odor of phenylisocyanate was noticeable. The mixture was then heated for three hours on the water-bath, when it was filtered and the ether evaporated spontaneously. A beautiful mass of prisms separated, which melted at about 65°. When crystallized from alcohol it formed colorless prisms and melted at 67° to 68°. A nitrogen determination gave:

	Calculated for $C_{16}H_{15}O_3N$.	Found.
N	5.20	5.38

Phenylimidoethyl benzoate and ethyl chlorcarbonate did not react at ordinary temperatures and no action was observed when the mixture was boiled. Finally a reaction took place on heating in a closed tube at 120° to 140° for six hours. When the tube was opened, ethyl chloride was evolved and an oil was obtained which deposited a solid on stirring with ether. This material formed prisms from alcohol, melted at 67°, and proved to be identical with that obtained in the above experiment. The substance is, therefore, benzoylphenylurethane, $C_6H_5N(COC_6H_5)CO_2C_2H_5$. When this is warmed with alcoholic sodium hydroxide, benzoic acid, and phenylurethane are obtained.

Benzanilideimide Chloride and Silver Anisate.—Four grams of benzanilideimide chloride and 5.1 grams of silver anisate were suspended in dry ether and allowed to stand for sixteen hours, when the ethereal solution gave no test for imide chloride. The ethereal solution was then filtered and spontaneously evaporated, whereupon a mass of long, slender, colorless prisms, mixed with some plates, was obtained. The mixture was washed with alcohol and the prisms crystallized from alcohol. They melted at 97° to 98°, were free from nitrogen, and on boiling with dilute alcoholic hydrochloric acid gave anisic acid. This material is therefore anisic anhydride, which is said to melt at 99°.[1]

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[1] Wheeler and McFarland: This JOURNAL, 18, 546 (1896). A sample of pure, dry formylbenzanilide, which originally melted at 112° and was a portion of the analyzed material, on keeping in a specimen-tube for seven years, was found to have decomposed quantitatively into benzanilide. The original prismatic shape of the crystals was retained, but they had become opaque and melted sharply at 162°.

When water was added to the alcoholic washings from the above, tables separated. These melted at 162° to 163°, after crystallizing several times from alcohol. This material was shown to be benzoylanisanilide by preparing the same substance from

Phenylimidoethyl Benzoate and Anisyl Chloride.—The anilide was obtained very smoothly by heating the mixture at 110° to 120° for six to seven hours. It was very soluble in alcohol and benzene and was purified by crystallizing from alcohol, from which it separated in six-sided tables and melted at 162° to 163°. When mixed with the above preparation the melting-point was not lowered. A nitrogen determination gave:

	Calculated for $C_{21}H_{17}O_3N$.	Found.
N	4.22	4.55

In another experiment the mixture of benzanilideimide chloride and silver anisate was boiled in ether for two and a half hours, when the reaction was complete. On evaporating the ether the residue consisted of prisms of anisic anhydride and a considerable amount of lozenge-shaped crystals. By fractional crystallization from alcohol a separation was effected and a compound melting at 171° was isolated. That this was not anisic anilide (also melting at 171°) was shown on mixing, whereupon the mixture melted at 148° to 155°. When mixed with the diacyl anilide, melting at 162° to 163°, it melted below 155°. A nitrogen determination agreed with the calculated for benzoylbenzenyldiphenylamidine:

	Calculated for $C_{26}H_{20}ON_2$.	Found.
N	7.4	7.7

Benzoylbenzenyldiphenylamidine was prepared for comparison by treating the amidine with benzoyl chloride. The product crystallized beautifully from alcohol, in the characteristic lozenge-shaped crystals, and melted at 171°. When mixed with the above the melting-point was not altered. This substance has recently been described by Lander.[1] He gives the melting-point at 170° to 172°.

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[1] Pisani: Ann. Chem. (Liebig), 102, 284.

Anisanilideimide Chloride, $CH_3OC_6H_4C(Cl)=NC_6H_5$, was prepared in the usual manner. It could not be distilled under diminished pressure without almost complete decomposition. A portion which distilled at 220° to 230° at 17 mm. pressure solidified on cooling, and when crystallized from petroleum ether formed colorless prisms, melting at 70°. With water it was converted into anisanilide, melting at 171,° which is said to melt at 168° to 169°.[2] A nitrogen determination gave:

	Calculated for $C_{14}H_{12}ONCl$.	Found.
N	5.7	6.0

Benzanilideimide chloride and silver m-nitrobenzoate in ether reacted with the greatest ease. In one hour the action was complete and a beautiful mass of colorless prisms had separated from the ethereal solution. Without purification they melted at 136°, and when crystallized from alcohol the melting-point did not rise beyond 139°. The compound was melted and recrystallized without altering the melting-point. When warmed with alkali, benzanilide was obtained. A nitrogen determination agreed with the calculated for *m*-nitrobenzoylbenzanilide, $C_6H_5CONC_6H_5.COC_6H_4NO_2$:

	Calculated for $C_{20}H_{14}O_4N_2$.	Found.
N	8.09	8.37

Labile Diacetylphenylurazole.—The silver salt of phenylurazole was prepared by Acree's directions and allowed to stand with one molecular proportion of acetyl chloride in cold dry benzene for three days. Heat was evolved when the silver salt and acid chloride were brought together. On spontaneously evaporating the benzene a beautiful mass of colorless prisms was obtained which, when rapidly heated, melted quite sharply at 113° to 115°. At about 120° the melted mass solidified again and did not melt completely until about 162°. This labile product was very soluble in benzene. On warming in this solvent and then precipitating with petroleum ether, material melting less sharply was obtained. A nitrogen determination was therefore made, using the original sample :

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[1] *Loc. cit.*

[2] Lossen: Ann. Chem. (Liebig), **175**, 292; Leuckart: J. prakt. Chem., **41**, 312.

	Calculated for $C_{10}H_9O_3N_3$.	Calculated for $C_{12}H_{11}O_4N_3$.	Found.
N	19.17	16.09	16.10

When this material was allowed to digest on the steam-bath in dilute alcohol it was converted into phenylurazole.

Stable Diacetylphenylurazole.—Some of the labile product was heated in an oil-bath at 120° to 140° for a short time. It melted and solidified again in the hot bath. On crystallizing then from alcohol it melted at 162°. This material proved to be identical with the diacetyl derivative described by Thiele, which we obtained according to his directions by heating the urazole with acetic anhydride. When the products were mixed the melting-point was not lowered. It was found that Thiele's diacetyl derivative could be crystallized from alcohol. A nitrogen determination, in the case of our material melting at 162°, gave :

	Calculated for $C_{12}H_{11}O_4N_3$.	Found.
N	16.09	16.5

When this diacetyl derivative was boiled with water it was converted into the monoacetyl derivative described by Thiele, which melted at 170°.

1-Phenyl-3,5-diethylurazole.—Eleven grams of silver phenylurazole and 6 grams of ethyl iodide were mixed in benzene and allowed to stand for thirty hours. The salt then appeared to be largely unaltered. Six grams more ethyl iodide were added and the mixture let stand for forty-eight hours longer. It was then filtered and the benzene was evaporated on the steam-bath. By boiling the silver residue with alcohol, phenylurazole was obtained. The amount represented about one-quarter of the urazole originally combined as silver salt. After evaporating the benzene an oil was obtained which finally solidified. This solid showed no definite melting-point. On treating the solid with cold ether the greater portion dissolved, leaving behind some phenylurazole. The ether extract was shaken thoroughly with alkali and washed, and then evaporated to dryness. The oil obtained soon solidified. The solidification took place by radiation from various points through the oil until the whole solidified to a botryoidal crystalline mass. When this cake, melting at 45° to 47°, was crystallized from ligroin it formed colorless needles which melted at 46° to 47°. Nitrogen determinations gave:

	Calculated for		Found.	
	$C_{10}H_{12}O_2N_3$.	$C_{12}H_{16}O_2N_3$.	I.	II.
N	20.59	18.02	17.85	18.07

The diethyl derivative insoluble in alkali and phenylurazole were the only products that we obtained in this reaction. The supposed mono-derivative of Acree was possibly a mixture of about equal parts of these compounds. Such a mixture would give results, on analysis, agreeing with those for a monoethyl derivative.

An analysis of the white silver salt used in the above experiment gave 39 per cent silver, while the calculated for a monosilver salt is 37.9 per cent. It is, in all probability, a monosilver salt. The fact that it gives a diacetyl and a diethyl derivative is a very curious result. In all probability a portion of the salt reacts with ethyl iodide on another portion in a manner similar to that observed by Lander[1] in the case of the action of silver oxide and alkyl halides on acid amides. It effects alkylation by combining with hydrogen iodide, which otherwise would be set free.

NEW HAVEN, CONN., February, 1903.

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[1] J. Chem. Soc. (London), 79, 698 (1901); 81, 591 (1902).

THE ACTION OF OZONE, HYDROGEN PEROXIDE, ETC., ON CARBON MONOXIDE.

BY WM. APP JONES.

In 1876 Remsen and Southworth[1] found that carbon monoxide is not oxidized by ozone, even when it is mixed with ozonized oxygen and placed in direct sunlight. The ozonizer used was of the form described by Wright.[2]

Baumann[3] showed that carbon monoxide is oxidized by the action of palladium hydrogen and oxygen.

Keiser,[4] repeating some unpublished work by Broun, found that there is no action upon carbon monoxide at the temperature at which the ozone is broken down by heat. No carbon dioxide is formed when the monoxide is passed through hydrogen peroxide which is being rapidly decomposed by heat. Leeds[5] and Baumann[6] state that the monoxide is oxidized by air and moist phosphorus. Keiser repeated this experiment but found no oxidation. There was a precipitation of barium carbonate in the baryta water, but this was shown to come from carbon in the phosphorus. No phosphorus compounds were found mixed with the barium carbonate.

In the course of his work Keiser confirmed the work of Traube,[7] who showed that carbon monoxide is changed to dioxide under the influence of palladium and hydrogen peroxide.

Theoretically, carbon monoxide is an unsaturated compound, and as such should readily combine with other substances. It unites directly with chlorine, and we would expect it to combine with oxygen without difficulty. The experiments briefly outlined above seem, on the whole, to show that such is not the case, but as there was still room for doubt it was suggested by Professor Remsen that the work be repeated, taking even greater precautions than ever before.

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[1] Remsen and Southworth: Am. J. Sci., [3], **11**, 136 (1876); Ber. d. chem. Ges., **8**, 1415.

[2] Wright: Am. J. Sci., [3], **4**, 26 (1872).

[3] Baumann: Ztschr. physiol. Chem., **5**, 244.

[4] This JOURNAL, **4**, 50, 454 (1882).

[5] Leeds: J. Am. Chem. Soc., **1**, 232.

[6] Baumann: Ztschr. physiol. Chem., **5**, 250.

[7] Traube: Ber. d. chem. Ges., **15**, 2854; **16**, 123.

The Action of Air and Carbon Monoxide on Moist Phosphorus.

These experiments were undertaken in order to see whether any carbon dioxide is formed by the passage of air and carbon monoxide over moist phosphorus. The apparatus used had no cork or rubber joints and contained no mercury, unlike the forms that had been used by previous workers. It consisted of a row of wash-bottles connected by fusing together their tubes.

At the very outset a serious difficulty was met with. No matter what the rate of flow of the air through the system of wash-bottles arranged thus, (1) KOH, (2) $Ba(OH)_2$, (3) P, (4) $Ba(OH)_2$, (5) KOH, although absolutely no precipitate appeared in 2, a decided deposit soon formed in bottle 4. By the time 8 or 10 liters of air had been passed, a precipitate 5 or 6 mm. deep had formed in the latter bottle.

It was soon found that when fresh phosphorus was introduced into 3, a very much larger precipitate was formed than when the air had been passed for about a day, and all the outside of the phosphorus had been burned off. Under these circumstances the precipitate in 4 was slight, but decided, and had a much more crystalline appearance than that of barium carbonate. It was at once suspected that some volatile compound of phosphorus had passed over, and this was found to be the case on testing the precipitate with ammonium molybdate. This same phenomenon was observed by Baumann,[1] but was not noted by Keiser.[2] In our case it was found necessary to introduce at least three wash-bottles, each containing about 10 cc. of pure water, between the bottle containing phosphorus and the one with the barium hydroxide. To show this we need only give the results of one experiment. After about 75 liters of air had been passed over the phosphorus and through a system of 4 wash-bottles, the contents of the latter were carefully transferred to beakers, treated with pure nitric acid, and warmed on a sand-bath in order to oxidize any phosphorus compound that might be present. The liquid was allowed to cool almost to the room tempera-

[1] Ztschr. physiol. Chem., 5, 250.

[2] This JOURNAL, 4, 454.

ture, and was then treated with a solution of ammonium molybdate in nitric acid, and the ammonium phosphomolybdate titrated according to the method of Kilgore.[1] The following results were obtained. The bottles are numbered in order after the one containing the phosphorus :

Bottle 1	required	8.7	cc. of N/7 alkali.
" 2	"	3.3	" " " "
" 3	"	0.6	" " " "
" 4	"	0.0	" " " "

These results show conclusively that some compound of phosphorus is carried over, and that several wash-bottles are required to remove it completely.

The apparatus finally used consisted of a series of wash-bottles fused together, and arranged as follows :

(1) KOH ; (2) $Ba(OH)_2$; (3) P ; (4) H_2O ; (5) H_2O ; (6) H_2O ; (7) $Ba(OH)_2$; (8) KOH.

About 25 or 30 grams of phosphorus were placed in 3, which contained about 10 cc. of water through which the gas passed in order to become thoroughly saturated immediately before coming in contact with the phosphorus. When new phosphorus was introduced air free from carbon dioxide was passed over it for a day to burn off the surface. This precaution was found to be absolutely necessary. A few of the results obtained are given :

1. Ten liters of air free from carbon dioxide were passed and found to give no precipitate in bottles 2 or 7. Then 6 liters of air containing approximately 3 liters of oxygen, 0.75 liter of carbon monoxide, and 4.25 liters of nitrogen were passed through. Time, six hours. The precipitate in 7 was rapidly filtered and washed, and then dissolved in dilute hydrochloric acid, and precipitated as barium sulphate. Found, 0.1664 gram $BaSO_4$, equivalent to 0.1406 gram $BaCO_3$, or 0.03143 gram CO_2. Three-fourths of a liter of carbon monoxide should yield 1.474 gram of carbon dioxide. Hence, the amount found is 2.13 per cent of the theoretical.

2. Air used, 9 liters ; carbon monoxide, 2.75 liters. Time,

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[1] J. Am. Chem. Soc., **16**, 765 ; **17**, 950.

twelve hours. In this case the weight of barium carbonate found was 0.1872 gram, corresponding to 0.03533 gram carbon dioxide, or 0.653 per cent of oxidation.

3. The barium carbonate was decomposed by dilute hydrochloric acid and the carbon dioxide liberated was absorbed in a weighed potash-bulb. Air used, 5 liters; carbon monoxide, 0.75 liter. The weight of carbon dioxide formed was 0.031 gram, corresponding to 2.102 per cent oxidation.

It will be noticed that, under the same conditions, the results are the same, practically, and, as Baumann pointed out, the amount of oxidation varies with the amount of phosphorus exposed and the rapidity of the current.

These experiments were tried repeatedly, but always with the same result. After 10 or 20 liters of air had been passed through the system and not the least trace of a precipitate had formed in the baryta bottle used as a test, a mixture of carbon monoxide and air was then passed through, all other conditions being the same. In no instance did a precipitate fail to appear in the baryta bottle after 2 or 3 liters of the mixture had been passed through. Further, every kind of change was made in the rate of flow, and the gases were mixed in the proportions given by Keiser,[1] and also by Baumann.[2] In every case there was evidence of oxidation.

The carbon monoxide was made from potassium ferrocyanide and also from formic acid.

Baumann,[3] in one experiment, introduced the carbon monoxide beyond the bottle containing the phosphorus. This experiment was repeated, the carbon monoxide being introduced between bottles 4 and 5. There was not the least trace of oxidation, thus confirming the result of Baumann. The odor of ozone was, however, distinctly perceptible at the end of the system of wash-bottles.

Hydrogen peroxide was also placed in 5, the monoxide being introduced between 4 and 5. Here, again, there was no evidence of oxidation.

[1] Keiser: This JOURNAL, 5, 454.

[2] Baumann: Ber. d. chem. Ges., 16, 2146.

[3] Baumann: Ztschr. phys. Chem., 5, 250.

The Action of Carbon Monoxide on Phosphorus in Hydrogen Peroxide.

The hydrogen peroxide was prepared by the method of Thomsen.[1] The solution was titrated with potassium permanganate and found to contain 2.424 per cent of hydrogen peroxide. The apparatus used is that described above. About 20 or 25 cc. of the pure peroxide was introduced into bottle 3, which contained 25 grams of phosphorus, the outside of which had been burned off. Before the potash bottle 1 was placed a series of wash-bottles containing an alkaline solution of pyrogallol, and the carbon monoxide used was collected in a gasometer over a similar solution. When the entire system had been filled with pure carbon monoxide, the solution of baryta water was introduced into bottle 7 and the experiment begun.

When the hydrogen peroxide and phosphorus came in contact there was not the least disturbance, and the occasional appearance of a bubble of gas on the phosphorus was the only indication of chemical action. The passage of pure carbon monoxide, about 0.75 to 1 liter per hour, was continued for thirty-six hours, and only a slight coating was observed on the inlet-tube, and no precipitate at all. This makes it appear extremely improbable that the oxidation of carbon monoxide by air and moist phosphorus is due to the action of the phosphorus on hydrogen peroxide, formed in the course of the experiment by the action of moist air on phosphorus.

When a strip of platinum was introduced into the bottle containing the phosphorus, there was, of course, oxidation of the carbon monoxide, and a quite rapid decomposition of the peroxide. This was pointed out by Traube.[2]

Repetition of the Work of Remsen and Keiser.

The work of Remsen and Keiser[3] was repeated according to the directions given by them, except that the wash-bottles were fused together instead of having ground-glass connections, and between the vessel containing the phosphorus over mercury and the last baryta bottle, three wash-bottles, each containing about 10 cc. of pure water, were introduced. As mentioned before, this was necessary in order to prevent some phosphorus compound from reaching the baryta bottle. It was also found necessary, whenever a new piece of phosphorus was used, to pass a current of air about a day to burn off the surface, for otherwise a large precipitate soon appeared in the baryta bottle. When these precautions were taken, 30 liters of air could be passed through the system without the least appearance of a precipitate in the test-bottle.

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[1] Thomsen : Ber. d. chem. Ges., **7**, 73.

[2] Traube : Ber. d. chem. Ges., **15**, 2325, 2854.

[3] Remsen and Keiser : This JOURNAL, **5**, 454.

One experiment is here described as performed : Eighteen liters, of air, free from carbon dioxide, were passed through the apparatus, the flow being so regulated that 2 or 3 bubbles passed per second. After the passage of this amount of air, absolutely no precipitate was to be seen in the test-baryta bottle, and only a very slight coating on the inlet-tube of the bottle. Without disturbing the apparatus, a mixture of carbon monoxide and air—2 liters of the monoxide to 22 liters of air—was passed through. After the passage of 5 or 6 liters of the mixture a decided precipitate had appeared in the test-baryta bottle, and when 12 liters had passed the precipitate was about 3 mm. deep and the inlet-tube became stopped up so as to prevent the flow of the gas.

Mixtures of air and carbon monoxide in various proportions were used, and the mixture was allowed to pass at different rates, but in all cases decided precipitates appeared in the test-bottle. In no case did the air, free from carbon dioxide, cause a precipitate.

Action of Ozone on Carbon Monoxide.

In view of the quite inexplicable statements that ozone does not oxidize carbon monoxide, either at the ordinary temperature or at 300° C., it was thought that possibly ozone more concentrated than that hitherto used might be able to cause oxidation.

The ozonizer used was of the Berthelot pattern, the air-space being about 30 cm. long, the outer and inner tubes being about 3 mm. apart. The diameter of the outer tube was 3 cm. The gas entered at the top of the outer tube and escaped from the bottom. The inner tube was filled with water slightly acidulated with sulphuric acid. The entire ozonizer was placed in a cylinder containing ice-cold, acidulated water. These two solutions were the electrodes. The strongest current used was from 12 bichromate cells arranged in series, the total voltage being about 18. The apparatus was arranged as shown in the figure on the opposite page.

A Ruhmkorff coil capable of giving a spark about 16 cm. long was used.

In making blank experiments with the oxygen the stopcock O was turned so that the carbon monoxide was excluded. The wash-bottle E prevented the entrance of air, and at all times kept the carbon monoxide from diffusing back into the ozonizer.

In most of the experiments quite a rapid current of oxygen was used in order to avoid the destruction of the ozone already formed.

Using all 12 cells and passing a current of 2 liters of air per hour, the ozone was passed directly into a solution of potassium iodide, and the liberated iodine was then titrated with a standard solution of sodium thiosulphate. As determined in this way, even with such a rapid current of oxygen, 3.78 per cent of ozone was formed. This ozone had an almost insufferable odor as it came from the apparatus, and a little of it, when inhaled, produced an irritation of the throat similar to that caused by chlorine. If conducted through a rubber tube it would eat through the rubber in a few minutes.

The results are as follows: Using 12 or even 6 cells connected with the coil, the carbon monoxide was oxidized at the ordinary temperature, and still more at 250° C. Using 2 cells, there was no oxidation at the ordinary temperature, but carbon dioxide was produced at 250°. Of course, thorough blank tests were made. The ozonized oxygen, when passed through the apparatus at the ordinary temperature or at 250° to 300°, did not produce a precipitate. The same was true of the carbon monoxide at the same temperatures. There can, therefore, be no doubt that the precipitation of barium carbonate,

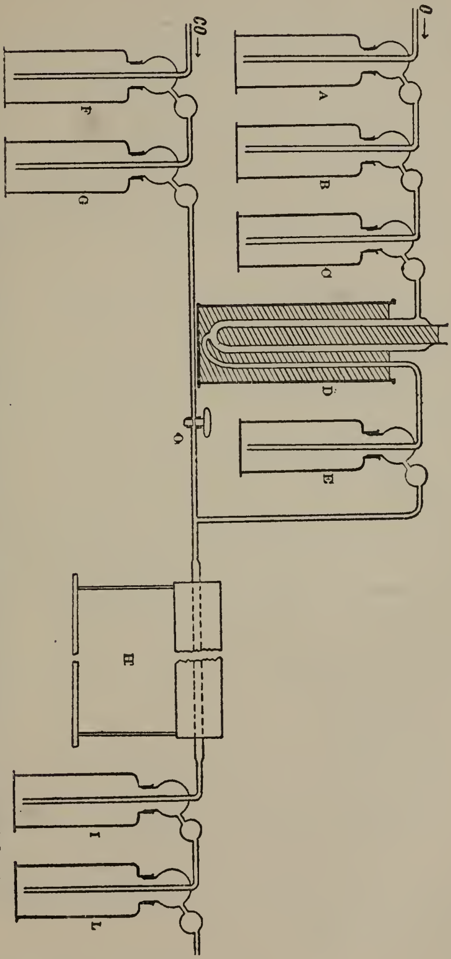

Fig. II.—Bottles A, B, F and L contained caustic potash solution; C, G and I, barium hydroxide; and E, distilled water.

which was carefully identified, was due to the action of the ozone on the carbon monoxide.

The action of the ozone formed by the oxidation of moist phosphorus was next tried at higher temperatures. Baumann[1] showed that it does not act on carbon monoxide at the ordinary temperature, a result confirmed by our work. Accordingly, about 30 or 40 grams of phosphorus were placed in the wash-bottle C, and the outside was carefully burned off. Then baryta water was introduced into the test-bottle. The ozone formed no precipitate. Then carbon monoxide was allowed to enter by opening the stop-cock O. After the passage of 12 liters of this mixture no precipitate appeared in the bottle containing baryta water. The temperature was then raised to 250° C. After the passage of about 2 liters, a precipitate began to form and increased slowly as the current of gas was continued. These experiments were repeated a number of times, always with the same result—a slight but distinct oxidation at 250°.

The oxidizing power of ozone varies with the temperature and the concentration.

The amount of ozone formed by the phosphorus when 2 liters were passed per hour was determined by passing it through a solution of potassium iodide, and titrating the iodine with standard thiosulphate solution. The percentage of ozone was found to be 0.0021, the ozonizer giving 3.78 per cent. These results show how little ozone is formed by the oxidation of moist phosphorus. The amount of ozone cannot be estimated by the odor, for the slightest trace of it will be quite perceptible.

The Action of Strong Hydrogen Peroxide on Carbon Monoxide.

Remsen[2] has shown that ordinary hydrogen peroxide does not oxidize carbon monoxide. This work was repeated, and it was found that a solution containing 2.424 per cent of hydrogen peroxide did not cause any oxidation. But since it was found that the oxidizing power of ozone depends on the

[1] Baumann: Ztschr. phys. Chem., 5, 250.

[2] Remsen: This JOURNAL, 4, 50.

concentration, it seemed advisable to prepare a much stronger solution of hydrogen peroxide, and to test its action.

The pure dilute solution of hydrogen peroxide was prepared according to the method of Thomsen,[1] and was then concentrated by the method of Wolffenstein.[2]

Three specimens of hydrogen peroxide of 53, 57, and 63 per cent strength, respectively, were prepared. No difficulties were encountered in obtaining the material, but precautions were taken in case an explosion should occur.

In the experiments a series of wash-bottles, with fused connections, was used. They were arranged in the following order:

(1) KOH; (2) $Ba(OH)_2$; (3) H_2O_2; (4) $Ba(OH)_2$; (5) KOH.

In each case the hydrogen peroxide was introduced into 3 and tested for several hours by passing a stream of air free from carbon dioxide in order to see that the material caused no precipitate in the test-baryta bottle 4. Then a current of pure carbon monoxide was passed. In no case was there the least evidence of oxidation of the monoxide.

The Action of Electrolytic Oxygen on Carbon Monoxide.

Since both Traube and Richarz have shown that some hydrogen peroxide and ozone are formed during the electrolysis of acidulated water, these experiments could give no evidence, unless negative in character,—if oxidation occurred it would not prove that electrolytic oxygen caused the oxidation, for platinum and hydrogen peroxide can act in the same way under the same circumstances. However, if no oxidation took place, it would show that electrolytic oxygen has not the power to oxidize carbon monoxide. This was found to be the case. For the electrolysis, a small U-tube holding only about 15 or 20 cc. was used, the object being to have very little water present to absorb the carbon dioxide that might be formed. The apparatus was arranged as follows:

$$\begin{tikzcd}
\text{(1) KOH} \arrow[r] & \text{(2) } Ba(OH)_2 \arrow[dr] & & \\
& & \text{U-tube} \arrow[r] & {} \\
\text{(3) KOH} \arrow[r] & \text{(4) } Ba(OH)_2 \arrow[ur] & & \\
& & \text{(5) } Ba(OH)_2 \arrow[r] & \text{(6) KOH.}
\end{tikzcd}$$

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[1] Thomsen: Ber. d. chem. Ges., 7, 73.

[2] Wolffenstein: *Ibid.*, 27, 3307. See also Spring: Ztschr. anorg. Chem., 8, 424; Brühl: Ber. d. chem. Ges., 28, 2847.

In making blank tests, air was passed through bottles 1 and 2 and into the U-tube, the inlet tube being curved and projecting down into the tube so that the gas might bubble directly against the electrode C, from which the oxygen was coming off. The wire connected with this electrode passed through a T-tube inserted in the stopper, and the gas left the U-tube through the side tube E. The negative electrode B, was connected in the same way, the hydrogen going out through the side tube D, and into a vessel containing a little alkali. Where the wire entered the T-tubes the top of the tube was tightly closed with melted paraffin so that there was no communication with the outer air, thus avoiding the absorption of carbon dioxide. In no case was there any evidence of oxidation of the carbon monoxide. When this gas was bubbled directly against the electrode C, from which large quantities of oxygen were being given off, there was not the slightest precipitate formed after twelve to fifteen hours.

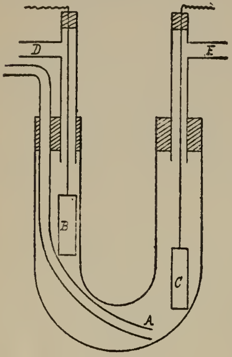

Fig. II.

JOHNS HOPKINS UNIVERSITY,
CHEMICAL LABORATORY, 1898.

THE ACTION OF OZONE ON CARBON MONOXIDE.

BY C. E. WATERS.

Because the results of Jones, which are given in the preceding article, are at variance with what had been previously stated in regard to the action of ozone on carbon monoxide, it was suggested by Prof. Remsen that the work be repeated, using a Holtz machine instead of the induction coil used by Jones. The same ozonizer was made use of, and the apparatus was arranged exactly as Jones had it, except that a wash-bottle containing sulphuric acid was placed just before the ozonizer, and the carbon monoxide was similarly dried before passing into the heated tube H. The Holtz machine was an instrument capable of giving very powerful discharges, and was run by means of an electric motor. It soon became evident that the condition of the weather had much to do with the results. On clear, dry days the speed of the motor had to be greatly reduced, and even then there was much leakage, in spite of the wires leading to the ozonizer being enclosed in glass tubes, and sparks frequently jumped around from the inner tube to the acidulated water in the outer cylinder. Under these conditions a precipitate was always formed in the bottle containing the barium hydroxide solution. During unfavorable weather the amount of oxidation was very slight. With the induction coil no such difficulty was met with, and Jones apparently obtained equally good ozone at all times. The form of ozonizer used was found to be much more efficient than the one previously used in some of this work.[1]

Some of our results are given below. Careful blank experiments were, of course, made, and in no case was there any evidence of oxidation. There was also no formation of carbon dioxide when the ozonized oxygen and the carbon monoxide were mixed at the ordinary temperature.

Experiment 1.—One liter of carbon monoxide and 3 liters of oxygen were used, the gases being mixed, after the oxygen was ozonized, in the tube H (see page 47). Temperature, 242°. There was a slight precipitate formed in I. In this experiment a Wright ozonizer was used.

Experiment 2.—Same arrangement as in 1. Temperature 269° to 272°. Two liters of carbon monoxide and 5 liters of oxygen. Time, three and a half hours. Only a very slight precipitate was formed.

Experiment 3.—The ozonizer used by Jones was substituted in this case, the rest of the apparatus remaining the same. Temperature, 278° to 282°. Three liters of carbon monoxide and 8 liters of oxygen. Time, four hours. At first there was almost no oxidation, but towards the last half of the experiment the machine worked much better, and a decided precipitate was formed.

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[1] Wright: Am. J. Sci., [3]. 4, 26 (1872).

Experiment 4.—Same as above. Temperature, 280°. With 1.25 liters of carbon monoxide and 3.5 liters of oxygen passing in about two hours, there were only traces of oxidation. The ozonizer was surrounded by ice.

Experiment 5.—One and a half liters of carbon monoxide and 6 liters of oxygen. The monoxide was not dried in this case, but was allowed to bubble through water just before mixing with the ozone. The ozonizer was surrounded by ice. Temperature, 280°. A slight precipitate soon formed, but did not perceptibly increase during the rest of the time.

Experiment 6.—The amount of ozone formed was determined by passing the gas into solutions of potassium iodide acidulated with dilute sulphuric acid, contained in bottles I and L. The solution was then titrated with a solution of sodium thiosulphate of known strength. The results are necessarily inexact, owing to the impossibility of accurately measuring the oxygen in a gas-holder.

Volume of oxygen, 5.5 liters. The iodine set free required 2.12 cc. of a solution of thiosulphate of such strength that 1 cc. was equivalent to 0.11506 gram iodine. Iodine found, 0.2439 gram, equivalent to 0.02938 gram ozone, or 0.37 per cent. In this experiment and the next a bottle containing an amount of acidulated potassium iodide solution equal to that used in I and L was allowed to stand beside these bottles. A certain amount of iodine was set free. The correction to be applied to I and L was determined by titrating with thiosulphate. During this experiment the machine did not work very well.

Experiment 7.—Everything arranged as in 6. Volume of oxygen, 4 liters. Two dishes containing strong sulphuric acid were placed in the case with the Holtz machine to dry the air, so that it worked up to its maximum efficiency. The iodine set free was 0.2877 gram, equivalent to 0.05444 gram ozone, or 0.95 per cent.

These figures do not agree very closely with those of Jones, but they go to show that the increased oxidation in dry weather is due to the greater amount of ozone formed. We think it may be fairly concluded that, although ozone does not act on carbon monoxide as readily as we should expect from its apparent unsaturation, still it does cause some oxidation to carbon dioxide, depending on the amount of ozone present in the oxygen. And, further, the oxidation does not take place to an appreciable extent at the ordinary temperature.

JOHNS HOPKINS UNIVERSITY,
May, 1903.

Contributions from the Chemical Laboratory of Harvard College.

ON CERTAIN NITRO DERIVATIVES OF THE VICINAL TRIBROMBENZOL.

BY C. LORING JACKSON AND A. H. FISKE.

The experiments described in this paper form a continuation of the work carried on for several years in this laboratory upon the behavior of benzol derivatives containing nitro groups and halogens. The 1-nitro-3,4,5-tribrombenzol, melting-point 112°, which was the first substance studied, was discovered by Körner,[1] and is easily prepared by treating paranitraniline with bromine and replacing with bromine the amino group in the dibromnitraniline thus obtained.

When treated with a dilute solution of sodic methylate, this 3,4,5-tribromnitrobenzol is converted into the dibromnitroanisol, melting at 122°, prepared by Körner[2] from the silver salt of the 2,6-dibrom-4-nitrophenol and methyl iodide. It follows from this that the atom of bromine in the para position to the nitro group has been replaced by the methoxyl group. This is what would be expected, as owing to its para position this atom is more exposed to the loosening effect of the nitro group than the other two atoms of bromine, which stand in the meta position to it. Staedel,[3] who prepared the substance according to Körner's method, gives the melting-point as 126° to 127°, evidently by an error of the press, as he says that the melting-point observed by him agrees with that of Körner, and gives the correct melting-point 122°.6 in the summary at the end of his paper.

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[1] Gazz. chim. ital., 4, 420 (1874).

[2] *Ibid.*, 4, 390 (1876). Körner gives the melting-point 122°.6.

[3] Ann. Chem. (Liebig), 217, 70 (1883).

By reduction with tin and hydrochloric acid this dibromnitroanisol was converted into the 2,6-dibrom-4-aminoanisol, which melts at 64° to 65°. Staedel obtained this substance in the same way, but gives no melting-point for it.

When the 3,4,5-tribromnitrobenzol was treated with a strong solution of sodic methylate it was converted into 4-methoxy-3,5-dibromazoxybenzol,

$$(CH_3O.C_6H_2Br_2)_2N_2O,$$

which melts at 214°. The easy formation of the azoxy compound in this case may be due to the fact that the two places ortho to the nitro group are occupied by hydrogen. In the other bromnitrobenzols studied in this laboratory the positions ortho to the nitro group were occupied by other radicals, and no formation of an azoxy compound has been observed, but many more experiments will be necessary before it can be determined whether this suggestion is entitled to consideration.

Sodic ethylate gave results similar to those obtained with the methylate. A strong solution of sodic ethylate formed the 4-ethoxy-3,5-dibromazoxybenzol, $(C_2H_5O.C_6H_2Br_2)_2N_2O$, which melts at 163°, and was obtained with more ease than the methyl compound. A weak solution of sodic ethylate converted the 3,4,5-tribromnitrobenzol into the 2,6-dibrom-4-nitrophenetol, $C_6H_2Br_2.NO_2.OC_2H_5$, which we found melts at 58° to 59°. Staedel,[1] on the other hand, assigns a melting-point of 108° to this substance. Accordingly, after we had settled the composition of our body by analysis, we determined its constitution by saponifying it, when we obtained a phenol, $C_6H_2Br_2.NO_2.OH$, which showed the melting-point 141° characteristic of the 2,6-dibrom-4-nitrophenol. Finally, in the hope of finding the cause of this difference between Staedel's result and ours, we prepared the dibromnitrophenetol according to Staedel's method, which consisted in making the dibromnitrophenol by treating paranitrophenol with bromine, and heating its silver salt with ethyl iodide; the 2,6-dibrom-4-nitrophenetol thus obtained melted at 58° to 59°, the melting-point of our sample prepared from the tribromnitrobenzol, and not at 108°, the temperature given by Staedel.

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[1] Ann. Chem. (Liebig), **217**, 67 (1883).

We are forced to the conclusion, therefore, that Staedel's melting-point, 108°, is incorrect.

By reduction with tin and hydrochloric acid our phenetol yielded the 2,6-dibrom-4-aminophenetol, $C_6H_2Br_2.NH_2.OC_2H_5$, which melted at 107°. Staedel gives the melting-point of this substance as 67°, so that the phenetol with the incorrect melting-point, 108°, gives a phenetidine also with an incorrect melting-point (67° instead of 107°). We can find no explanation for these differences between Staedel's melting-points and ours.

The dibromnitrophenetol was converted into the 4-ethoxy-3,5-dibromazoxybenzol already mentioned, when it was boiled with a strong alcoholic solution of sodic ethylate.

When the 3,4,5-tribromnitrobenzol was boiled for some time with an aqueous solution of sodic hydrate, the 2,6-dibrom-4-nitrophenol was formed. Alcoholic ammonia converted the tribromnitrobenzol into 2,6-dibrom-4-nitraniline, as was proved by Körner.[1] With aniline, even at its boiling-point, the 3,4,5-tribromnitrobenzol seemed to enter into no reaction, as it was recovered afterward unchanged. Sodic acetoacetic ester also had no apparent action on it. Sodic malonic ester formed with it a red salt, which was not studied.

When boiled with a mixture of fuming nitric acid and strong sulphuric acid, the 3,4,5-tribromnitrobenzol was converted into a dinitro compound, $C_6HBr_3(NO_2)_2$, which must have the structure $Br_3 3,4,5.(NO_2)_2 1,2$. It melts at 160° and is much more reactive than the mononitro compound. With sodic methylate, in the cold, it gave a tribromnitroanisol, $C_6HBr_3.NO_2.OCH_3$, by the replacement of a nitro group by a methoxy group. This melts at 109° to 110°. If a boiling solution of sodic methylate in methyl alcoholic acted on the tribromdinitrobenzol, a dibromnitrodimethoxybenzol, $C_6HBr_2.NO_2.(OCH_3)_2$, melting at 81°, was formed by the replacement of an atom of bromine and a nitro group by methoxy groups. When the tribromdinitrobenzol was treated with an alcoholic solution of sodic ethylate in the cold, the tribromnitrophenetol, $C_6HBr_3.NO_2.OC_2H_5$, melting at 74°, was formed. The experiment with a boiling solution of sodic ethylate led only to tarry products.

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[1] Gazz. chim. ital., 4, 421 (1874).

On boiling the 3,4,5-tribrom-1,2-dinitrobenzol with a 10 per cent solution of sodic hydrate a phenol, $C_6HBr_3.NO_2.OH$, was formed, which melted at 120° to 121°. As this gave the anisol, melting at 109° to 110°, when its silver salt was treated with methyl iodide, it must have the same structure as anisol.

Alcoholic ammonia in the cold replaced a nitro group by an amino group, forming a tribromnitraniline, $C_6HBr_3.NO_2.NH_2$, melting at 161°. If the two materials were heated to 100°, a diamino compound, $C_6HBr_2.NO_2(NH_2)_2$, melting at 189° to 190°, was obtained. Neither of these substances gave salts, even when their solutions in benzol were treated with gaseous hydrochloric acid. Boiling aniline produced a substitution of the nitro group by the anilino radical, giving

$$C_6HBr_3.NO_2.C_6H_5NH,$$

melting at 138° to 139°.

The 3,4,5-tribrom-1,2-dinitrobenzol upon reduction with tin and hydrochloric acid, gave the 3,4,5-tribromorthophenylenediamine, $C_6HBr_3(NH_2)_2$, melting at 91°, which formed a salt with 1 molecule of hydrochloric acid, $C_6HBr_3.NH_2.NH_3Cl$. With phenanthrenequinone it gave 3,4,5-tribromdiphenylenequinoxaline (or 3,4,5-tribromphenanthrophenazine),

$$C_6HBr_3N_2C_2C_{12}H_8,$$

which did not melt below 300°. With benzil it gave 3,4,5-tribromdiphenylquinoxaline, $C_6HBr_3N_2C_2C_{12}H_{10}$, a brick-red powder.

Of these derivatives of the 3,4,5-tribrom-1,2-dinitrobenzol the constitution of the tribromnitraniline is established, since there are only two formulas which it is possible to assign to it—$NH_2 1, Br_3 2,3,4, NO_2 6$ and $NH_2 1.Br_3 3,4,5.NO_2 2$—and a substance having the second of these was made by Gallivan and one of us[1] by introducing a nitro group into the 3,4,5-tribrom aniline. As this substance melts at 130°, and ours at 161°, it follows that the first of these structures belongs to our compound, which is therefore the 2,3,4-tribrom-6-nitraniline. An attempt to connect the tribromnitrophenol and its ethers with this tribromnitraniline by means of the diazo reaction gave a phenol closely resembling that made directly from the tribromdinitrobenzol, but owing to a mistake in the work the identity of the two substances was not established with certainty. Unfortunately, this mistake was not discovered until it was too late to correct it. We cannot, therefore, present an experimental proof that the nitro group replaced by the hydroxyl is the same as that replaced by the amino group, but we are of the opinion that the following considerations leave little doubt that this is the case. In the 3,4,5-tribrom-1,2-dinitrobenzol, both nitro groups are exposed to the loosening effects of a nitro group in the ortho and an atom of bromine in the para position, but, while the nitro group 1 is but little effected by the third atom of bromine in the meta position, the nitro group 2 is exposed to the marked loosening effect of an atom of bromine in the ortho position, and, therefore, should be the one replaced in all these reactions.

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[1] This JOURNAL, **20**, 184 (1898).

If this reasoning is admitted, these substances receive the following names: 2,3,4-tribrom-6-nitroanisol, melting-point 109° to 110°; 2,3,4-tribrom-6-nitrophenetol, melting-point 74°; 2,3,4-tribrom-6-nitrophenol, melting-point 120° to 121°; 2,3,4-tribrom-6-nitrodiphenylamine, melting-point 138° to 139°.

The nitro group replaced by the methoxy radical in forming $C_6HBr_2.NO_2(OCH_3)_2$ must be that standing at 2 in the 3,4,5-tribrom-1,2-dinitrobenzol, as this substance can be made by treating the tribromnitroanisol with boiling sodic methylate solution. It follows then, without much doubt, that the atom of bromine substituted is that standing at 4, since the other two atoms of bromine stand in the meta position to the nitro group, when the dimethoxy body is made from the anisol. It should be called, therefore, 2,4-dibrom-6-nitroresorcine dimethyl ether, melting-point 81°.

A similar course of reasoning would show that the constitution of the diamino body is 2,4-dibrom-6-nitrometaphenylenediamine, and this result is confirmed by our observation that it did not give the characteristic quinoxaline test for an orthodiamine, or the Lauth violet test for a paradiamine. It may be objected that these tests might not act with a body containing so many negative groups, but we cannot think this objection of much weight in view of the facts that a quinoxaline was formed easily from 3,4,5-tribromorthophenylenediamine, as described in this paper, and that the 1,4-dibrom-2,5-phenylenediamine gave the Lauth violet test without difficulty.[1]

The most striking observation made in the work with the tribromdinitrobenzol is that the nitro group is replaced more easily than the atom of bromine—certainly an unexpected result—in fact the reactions already described, which take place in the cold, are almost exclusively confined to the substitution of the nitro group, but this cannot be accepted as a general rule, since sodic malonic ester in the cold gave a substance with the formula $C_6HBr_2(NO_2)_2CH(COOC_2H_5)_2$, to judge from a single determination of bromine, and was, therefore, made by the replacement of an atom of bromine by the malonic ester radical.

EXPERIMENTAL PART.

Preparation of 3,4,5-Tribromnitrobenzol.

Paranitraniline was converted into the dibromparanitraniline by the method of Körner.[2] For this purpose 15 grams of the paranitraniline were dissolved in rather more than 50 grams of ordinary strong hydrochloric acid, and the solution diluted to 2 liters. A stream of air loaded with bromine vapor was then passed through this solution until a permanent red color was imparted to it. The precipitate, after washing, was nearly pure dibromnitraniline, as it melted at 200° to 201° instead of 202°.5. Yield, from 80 to 90 per cent of the theoretical.

The amino group in the dibromnitraniline was next replaced by bromine as follows: Twenty grams of the dibromnitraniline (melting-point 202°) were mixed with 70 cc. of hydrobromic acid (sp. gr. 1.35, b. p. 124° to 126°) and the thin paste thus formed was treated with sodic nitrite in a 500 cc. flask, which was loosely corked, care being taken by shaking the flask occasionally to expose as large a surface of the mixture as possible to the action of the nitrous fumes. Pieces of the sodic nitrite were added from time to time so as to keep the flask constantly filled with red fumes, and the operation was carried on until the color of the paste had changed from yellow to red, which commonly took place at the end of three or four days. A quantity of hydrobromic acid was then added and the mixture boiled until it ceased to give off red fumes. This treatment converted the red solid into a dark-brown oil, which was separated from the hydrobromic acid, and, after it had hardened, washed and dried at ordinary temperatures. To purify the crude tribromnitrobenzol thus obtained it was dissolved in benzol and the solution boiled with bone-black for half an hour in a flask with a return-condenser, after which it was filtered, allowed to cool, and any yellow solid which separated removed by a second filtration. The filtrate was freed from benzol as completely as possible by distillation on the steam-bath, and the residue stirred while it was cooling so as to get small crystals. These were filtered from the mother-liquor, washed with a small quantity of cold alcohol, and recrystallized from hot alcohol until they melted at 112°. The yield averaged nearly 80 per cent of the theoretical.

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[1] This JOURNAL, 28, 461.

[2] Gazz. chim. ital., 4, 346 (1874).

Action of Sodic Methylate in the Cold on 3,4,5-Tribromnitrobenzol.

2,6-Dibrom-4-nitroanisol, $C_6H_2Br_2.NO_2.OCH_3$.—Five grams of the 3,4,5-tribromnitrobenzol were mixed with the solution of sodic methylate in methyl alcohol, formed by acting on 0.8 gram of sodium with 25 cc. of methyl alcohol, that is, a little more than 2 molecules of the methylate to each molecule of the tribromnitrobenzol. The mixture was allowed to stand two days in a corked flask, when it was found that the liquid had turned yellow, and deposited crystals. The yellow mother-liquor, on dilution with water, gave a white precipitate, which was filtered out and added to the crystals. In the aqueous filtrate a strong test for a bromide was obtained, but none for a nitrite. The organic product of the reaction was purified by recrystallizing it from hot methyl alcohol until it showed the constant melting-point 122°, which indicated that it was the dibromnitroanisol, $OCH_31.Br_22,6.NO_24$, melting at 122°.6, that was made by Körner[1] from the silver salt of the 2,6-dibrom-4-nitrophenol and methyl iodide. This result was confirmed by saponifying our substance with sulphuric acid, when it yielded this 2,6-dibrom-4-nitrophenol, as shown by the melting-point 141°.

4-Methoxy-3,5-dibromazoxybenzol.—This substance was obtained when the 3,4-tribromnitrobenzol was treated with a much stronger solution of sodic methylate than that used in making the dibromnitroanisol. Four grams of the tribromnitrobenzol were mixed with the sodic methylate made from 2.4 grams of sodium and 20 cc. of methyl alcohol,[2] that is, over 9 molecules of the methylate to each molecule of the tribromnitrobenzol. The mixture was boiled in a flask with a return-condenser for six hours, after which the product consisted of a solid suspended in a dark-red liquid. The solid was filtered out, washed repeatedly with water, and then with boiling alcohol to remove any 2,6-dibrom-4-nitroanisol which had been formed, and the residue recrystallized from hot benzol till it showed the constant melting-point 214°. Another excellent method of purifying the substance consisted in dissolving it in chloroform and then precipitating out the solid with an excess of alcohol. The compound was dried at 100° and analyzed with the following results:

I. 0.2034 gram substance gave 0.2156 gram CO_2 and 0.0382 gram H_2O.

II. 0.3305 gram substance gave 0.3470 gram CO_2 and 0.0668 gram H_2O.

III. 0.2433 gram gave, by the Carius method, 0.3200 gram AgBr.

IV. 0.2065 gram substance gave 0.2714 gram AgBr.

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[1] Gazz. chim. ital., 4, 390 (1874).

[2] Good results were also obtained with 3 grams of sodium and 40 cc. of methyl alcohol.

V. 0.2014 gram substance gave, by the method of Zeisel, 0.1550 gram AgI.

	Calculated for $[C_6H_2Br_2.OCH_3]_2N_2O$.	Found. I.	II.	III.	IV.	V.
C	29.27	28.92	28.64	....	....	....
H	1.74	2.09	2.25	....	....	....
Br	55.75	....	....	55.98	55.93	....
CH_3O	10.80	....	....	....	....	10.15

The substance is, therefore, the 4-methoxy-3-5-dibromazoxybenzol. The formation of this substance depended on the strength of the sodic methylate solution used and not on the fact that the mixture was boiled, as a mixture of the tribromnitrobenzol, even after boiling for two days with a more dilute solution of sodic methylate, gave only the dibromnitroanisol, melting at 122°, with some of the corresponding phenol melting at 141°. On the other hand, the azoxy compound was formed when the mixture of the tribromnitrobenzol and the stronger solution of sodic methylate was allowed to stand in the cold. In every case some of the dibromnitroanisol was formed also, which was obtained from the filtrate and the alcoholic washings. The filtrate also gave a test for a bromide but none for a nitrite.

The methoxydibromazoxybenzol was also made from the dibromnitroanisol, melting at 122°, by boiling a mixture of 3 grams of the anisol and the sodic methylate from 2.25 grams of sodium and 30 cc. of methyl alcohol. After the mixture had been boiled for three hours in a flask with a return-condenser, it was precipitated with water and the precipitate boiled with alcohol to remove any unaltered anisol, when the residue, insoluble in alcohol, showed the melting-point of the azoxy compound, 214°.

Properties of the 4-Methoxy-3,5-bromdiazoxybenzol, $(C_6H_2Br_2.OCH_3)_2N_2O$.—It crystallizes from benzol in radiating, brush-like bundles of yellowish-white needles. It melts at 214° and is easily soluble in chloroform; soluble in benzol; slightly soluble in acetone or glacial acetic acid; nearly insoluble in methyl alcohol or ether; essentially insoluble in alcohol, ligroin, or water, whether hot or cold. It is insoluble in strong hydrochloric acid. A specimen of the substance was found to be unchanged after it had been boiled for four days with a solution of stannous chloride, strong hydrochloric acid, and tin. Aluminium and sodic hydrate also seemed to have no action on it. On the other hand, zinc dust and acetic acid seemed to reduce it, although we did not succeed in isolating the product, and with hydriodic acid it underwent a decomposition reaching apparently to the destruction of the benzol rings.

Reduction of the 2,6-Dibrom-4-nitroanisol (2,6-Dibrom-4-aminoanisol).—One gram of the dibromnitroanisol was mixed with about 10 cc. of a solution of stannous chloride prepared from 2 grams of tin, a little granulated tin, and 10 cc. of strong hydrochloric acid, and the mixture was boiled for six hours in a flask with a return-condenser. At the end of this time all the organic matter had gone into solution, and on cooling, a double tin salt in large white flakes crystallized out so freely that the mixture became almost solid. These crystals were filtered out, washed with very little cold water, dissolved in a few cc. of hot water, and the boiling solution treated with an excess of sodic hydrate. A white precipitate was formed in this way, which melted partially in the boiling water. This was filtered out, washed, and after drying for a few minutes boiled out with ligroin (boiling between 70° and 90°), the ligroin extract was filtered hot, and on cooling deposited white crystals of the anisidine, which were recrystallized from ligroin until they showed the constant melting-point 64° to 65°. An additional amount of the substance was obtained by extracting the sodic hydrate solution with ligroin. It was dried *in vacuo* and analyzed with the following result:

0.1251 gram substance gave, by the Carius method, 0.1679 gram of argentic bromide.

	Calculated for $C_6H_2Br_2.NH_2.OCH_3$.	Found.
Br	56.94	57.14

This dibromanisidine has been prepared by Staedel,[1] but he did not give its melting-point, or a full description of its properties, which we have observed as follows: It crystallizes from cold alcohol in rather short, white prisms, sometimes terminated by a basal plane, more often by several planes at a very obtuse angle to each other. It melts at 64° to 65°, and is easily soluble in ethyl or methyl alcohol, ether, benzol, chloroform, acetone, or carbonic disulphide; soluble in glacial acetic acid; slightly soluble in cold ligroin, freely soluble in hot ligroin; insoluble in water. The best solvent for it is ligroin.

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[1] Ann. Chem. (Liebig), **217**, 71 (1883).

For further identification we prepared and analyzed the chloride. For this purpose 0.3 gram of the anisidine, dissolved in 100 cc. of dry benzol, was treated with hydrochloric acid gas. The white precipitate thus obtained was washed with dry benzol, dried *in vacuo*, and analyzed with the following result:

0.2120 gram substance gave, by the Carius method, 0.3446 gram of the mixture of AgCl and AgBr.

	Calculated for $C_6H_2Br_2.OCH_3NH_3Cl$.	Found.
Cl + Br	61.57	61.18

Staedel prepared this chloride, and also the sulphate and oxalate of this dibromanisidine.

Action of Sodic Ethylate on 3,4,5-Tribromnitrobenzol.

2,6-Dibrom-4-nitrophenetol, $C_6H_2Br_2.OCrH_5.NO_2$.–Two grams of the 3,4,5-tribromnitrobenzol dissolved in 5 cc. of benzol were mixed with a solution of sodic ethylate made from 0.5 gram of sodium and 30 cc. of absolute alcohol, and the mixture was allowed to stand at ordinary temperatures for four or more days, after which the brown solution was diluted with a quantity of water and the precipitate washed and purified by crystallization from alcohol, with the aid of bone-black, until it showed the constant melting-point 58° to 59°, when it was dried *in vacuo* and analyzed with the following result:

I. 0.1230 gram substance gave, on combustion, 0.1322 gram CO_2 and 0.0348 gram H_2O.

II. 0.3036 gram substance gave, by the Carius method, 0.3491 gram AgBr.

	Calculated for $C_6H_2Br_2.OC_2H_5NO_2$.	Found. I.	II.
C	29.54	29.32	....
H	2.15	3.16	....
Br	49.23	....	48.93

The yield was essentially quantitative.

Properties of the 2,6-Dibrom-4-nitrophenetol.—It crystallizes from alcohol in long, tapering, very sharp, white needles arranged in radiating groups, and showing a tendency to branch. It melts at 58° to 59°, and is very soluble in ether, benzol, chloroform, or acetone; fairly soluble in hot, less soluble in cold ethyl alcohol; somewhat more soluble in methyl than in ethyl alcohol; soluble in ligroin; essentially insoluble in water. Alcohol is the best solvent for it.

Staedel[1] has prepared a 2,6-dibrom-4-nitrophenetol, which he found melted at 108°. Our compound, which should have the same structure, melts at 58° to 59°. Our analyses leave no doubt that it is a dibromnitrophenetol, but, as it is possible to form two different dibromnitrophenetols from the 3,4,5-tribromnitrobenzol ($OC_2H_51.Br_22,6.NO_24$ and $OC_2H_51.Br_22,3.NO_25$), we determined the constitution of our substance as follows: A quantity of the dibromnitrophenetol was saponified by boiling it in a flask with a return-condenser with sulphuric acid of sp. gr. 1.44. The phenol thus obtained, after recrystallization from benzol, melted at 141°, the melting-point of the 2,6-dibrom-4-nitrophenol. There can be no doubt, therefore, that our compound is the 2,6-dibrom-4-nitrophenetol. This 2,6-dibrom-4-nitrophenol was the substance from which Staedel prepared his phenetol, melting at 108°, and accordingly we repeated Staedel's work to see if we could find the reason for the difference between the melting-points observed by him and by us. For this purpose we made the 2,6-dibrom-4-nitrophenol by the action of bromine vapor upon the 4-nitrophenol dissolved in a large quantity of water. The product, which showed the correct melting-point 141°, was converted into the potassium salt with potassic carbonate, and a solution of this precipitated with argentic nitrate to form the silver salt. The dried silver salt was heated to 100° for eight hours in a sealed tube with ethyl iodide. The product, mixed with some alcohol, was poured off from the argentic iodide, and on evaporation yielded crystals of the 2,6-dibrom-4-nitrophenetol, which melted at 58° to 59°, like that prepared by us from 3,4,5-tribromnitrobenzol. As in this experiment we had followed the method of Staedel as carefully as possible, we are forced to conclude that he is in error in ascribing the melting-point 108° to the 2,6-dibrom-4-nitrophenetol.

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[1] Ann. Chem. (Liebig). **217**, 67 (1883).

4-Ethoxy-3,5-dibromazoxybenzol, $(C_6H_2Br_2.OC_2H_5)_2N_2O$. — This substance was obtained when the 3,4,5-tribromnitrobenzol was treated with a much stronger solution of sodic ethylate than that which yielded the phenetol. Heating the mixture promotes the formation of the azoxy compound, but, as the product in this case is very impure, it is wiser to carry on the preparation in the cold. Occasionally this compound was formed even with the dilute solutions of the ethylate, which usually gave the phenetol. We have not succeeded in discovering the cause of this abnormal behavior. The best method for preparing this substance was as follows: Ten grams of 3,4,5-tribromnitrobenzol were mixed with the sodic ethylate made from 3.5 grams of sodium and 60 cc. of absolute alcohol, and the mixture allowed to stand in a corked flask at ordinary temperatures for three or more days. The dark-brown liquid thus obtained was diluted with water, and the precipitate, after washing with water, was extracted with a small amount of alcohol to remove any phenetol which might have been formed. The residue was then extracted several times with ligroin, which dissolved the azoxy body, thus separating it from the dark-colored, tarry impurities. It was purified by crystallization from ligroin or benzol until it showed the constant melting-point 163°, when it was dried at 100° and analyzed with the following results:

I. 0.1983 gram substance gave, on combustion, 0.2262 gram CO_2 and 0.0569 gram H_2O.

II. 0.1974 gram substance gave, by the Carius method, 0.2467 gram AgBr.

III. 0.2569 gram substance gave, by the Carius method, 0.3202 gram AgBr.

	Calculated for $(C_6H_2Br_2OC_2H_5)_2N_2O$.	Found. I.	II.	III.
C	31.89	31.91	....	....
H	2.32	3.27	....	....
Br	53.15	....	53.22	53.07

The dibromethoxyazoxybenzol can also be prepared from the dibromnitrophenetol melting at 58° to 59° by boiling it for half an hour with a strong solution of sodic ethylate (0.25 gram of sodium and 30 cc. of alcohol to 1 gram of the phenetol).

Properties of the 3,5-Dibrom-4-ethoxyazoxybenzol.—It crystallizes from benzol in long, very slender, yellowish-white needles, which melt at 163°. It is soluble in benzol or chloroform; slightly soluble in alcohol, methyl alcohol, ether, glacial acetic acid, or ligroin. The best solvent for it is benzol. Sodic hydrate in aqueous solution decomposes it only to a slight extent, even when boiled with it for some time. It forms no salt with hydrochloric acid, which is without action on it even when boiling.

Reduction of the 2,6-Dibrom-4-nitrophenetol (2,6-Dibrom-4-aminophenetol), $C_6H_2Br_2.OC_2H_5.NH_2$.—Three grams of the 2,6-dibrom-4-nitrophenetol were mixed with 15 cc. of the solution of stannous chloride made from 3 grams of tin. Some pieces of tin and a little strong hydrochloric acid were added, and the mixture boiled in a flask with a return-condenser until almost the whole of the phenetol had gone into solution. The solution was filtered hot to get rid of the tin, and the filtrate, on cooling, became filled with white crystals, probably of a double tin salt. These were filtered out and boiled with water and a little sodic hydrate for a few minutes, and the precipitate filtered off after it had solidified on cooling. The filtrate from the crystals treated in the same way gave an additional quantity of the base. The sodic hydrate filtrates, on extraction with ether, gave so little of the base that this treatment is not worth while. The two precipitates were extracted repeatedly with ligroin to separate the organic matter from hydrate of tin, and the extract purified by crystallization from ligroin until it showed the constant melting-point 107°, when it was dried *in vacuo* and analyzed with the following result :

0.1338 gram substance gave, by the Carius method, 0.1710 gram AgBr.

	Calculated for $C_6H_2Br_2.OC_2H_5.NH_2$.	Found.
Br	54.24	54.38

Properties of the 2,6-Dibrom-4-aminophenetol.—It crystallizes from alcohol in broad, white plates terminated by two planes at an acute angle to each other, with the angle truncated by a basal plane. It melts at 107°. It is freely soluble in benzol, ether, or acetone ; soluble in alcohol or chloroform ; nearly insoluble in cold, soluble in hot ligroin. Alcohol is the best solvent for it.

The chloride of the base was prepared by passing hydrochloric acid gas into its solution in benzol. The precipitate was washed with benzol, dried *in vacuo*, and analyzed with the following result :

0.2056 gram substance gave, by the Carius method, 0.3175 gram mixture of AgCl and AgBr.

	Calculated for $C_6H_2Br_2.OC_2H_5.NH_3Cl$.	Found.
Cl + Br	58.98	58.11

Staedel,[1] who discovered this dibromphenetidine, gives its melting-point as 67°, whereas we observed it as 107°. The analyses and methods of preparation establish the identity of these two bodies beyond a doubt. We are no more able to explain the difference between the melting-points observed by Staedel and by us than in the corresponding case of the dibromnitrophenetol from which the dibromphenetidine was prepared, where Staedel gives the melting-point 108°, but we found 58° to 59°.

Upon boiling the 3,4,5-tribromnitrobenzol with water containing a little potassic carbonate for sixteen hours very little action was observed. The amount of phenol formed was too small for identification, and most of the original substance was recovered unaltered. When the 3,4,5-tribromnitrobenzol was boiled with sodic hydrate, on the other hand (1 gram tribromnitrobenzol, 1 gram of sodic hydrate, and 10 cc. of water), for sixteen or more hours, a considerable quantity of the 2,6-dibrom-4-nitrophenol was formed, which was recognized by its melting-point, 141°. Sodic malonic ester seems to react with the 3,4,5-tribromnitrobenzol, as a red substance was formed, but, even after long standing or boiling with a return-condenser, most of the original substance was recovered unaltered. The same remark applies with even greater force to the action of sodic acetoacetic ester. Aniline also, even at its boiling-point, showed little or no action on the 3,4,5-tribromnitrobenzol, which was recovered from the mixture with unaltered melting-point.

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[1] Ann. Chem. (Liebig), **217**, 72.

3,4,5-Tribrom-1,2-dinitrobenzol, $C_6HBr_3(NO_2)_2$.

To prepare this substance 50 grams of the 3,4,5-tribromnitrobenzol were mixed with 200 cc. of fuming nitric acid and 50 cc. of strong sulphuric acid, and the mixture heated, in a flask closed with a porcelain crucible, to a temperature just below its boiling-point for two hours. At the end of this time a considerable quantity of solid had separated, but, disregarding this, the heating was continued for half an hour longer, and then the product was poured into a large quantity of cold water, and allowed to stand over night. The precipitate was filtered out, and proved pure enough for use in other preparations. The yield was essentially quantitative. For analysis, it was purified by crystallization from alcohol until it showed the constant melting-point 160°, when it was analyzed with the following result:

0.1700 gram substance gave, by the Carius method, 0.2372 gram AgBr.

	Calculated for $C_6HBr_3(NO_2)_2$.	Found.
Br	59.26	59.39

Properties of 3,4,5-Tribrom-1,2-dinitrobenzol.—It forms large, well-formed, yellowish-white prisms, terminated by many planes and apparently belonging to the monoclinic system.

It melts at 160°, and is freely soluble in benzol, chloroform, acetone, or glacial acetic acid; soluble in hot ethyl or methyl alcohol, or ether, slightly soluble in these solvents when cold; slightly soluble in hot, even less so in cold ligroin; essentially insoluble in water. An attempt was made to convert it into the trinitro body by treatment with fuming sulphuric and nitric acids, and, although no definite result was obtained, the indications of the experiment were so favorable that this subject will be taken up hereafter in this laboratory.

Action of Cold Sodic Methylate on the 3,4,5-Tribrom-1,2-dinitrobenzol.

2,3,4-Tribrom-6-nitroanisol, $C_6HBr_3.NO_2.OCH_3$.—A dilute solution of sodic methylate was prepared by adding 1 gram of sodium to 200 cc. of methyl alcohol. After this had cooled, 10 grams of the powdered tribromdinitrobenzol were added and the mixture allowed to stand at ordinary temperatures with frequent shaking. In half an hour the liquid became filled with needles, which were filtered out, washed with water, and recrystallized from hot alcohol until they showed the constant melting-point 109° to 110°. The wash-water gave a test for a nitrite but none for a bromide. It also seemed to contain a small quantity of the salt of a phenol, as it was yellow, and gave a trace of a precipitate when acidified. The new organic substance melting at 109° to 110° was dried *in vacuo* and analyzed with the following results:

I. 0.2012 gram substance gave, by the Carius method, 0.2920 gram AgBr.

II. 0.2954 gram substance gave 0.4290 gram AgBr.

	Calculated for $C_6HBr_3.NO_2.OCH_3$.	Found. I.	II.
Br	61.38	61.77	61.81

Properties of 2,3,4-Tribrom-6-nitroanisol.—It crystallizes from alcohol in matted spherical masses of very slender, radiating white needles, which melt at 109° to 110°. It is freely soluble in ether, benzol, chloroform, or acetone; slightly soluble in ethyl or methyl alcohol, glacial acetic acid, or ligroin; essentially insoluble in water. We did not succeed in saponifying it by boiling it with sulphuric acid of sp. gr. 1.44.

Action of Boiling Sodic Methylate on 3,4,5-Tribrom-1,2-dinitrobenzol.

Dimethoxydibromnitrobenzol, $C_6HBr_2.NO_2(OCH_3)_2$. — Two grams of the tribromdinitrobenzol were mixed with the solution of sodic methylate made from 0.25 gram of sodium and 25 cc. of methyl alcohol, and the mixture boiled for an hour in a flask with a return-condenser. Upon pouring the product into water a yellow precipitate was obtained which was purified by recrystallization from alcohol. In most cases it was found necessary to start this crystallization by the introduction of a little of the solid. The aqueous liquid gave a test for a nitrite and for a bromide, and also contained the salt of a phenol, to judge from its yellow color and a slight precipitate when acidified, but the amount was too small for identification. The principal product lost its yellow color on recrystallization and melted constant at 81°, when it was dried *in vacuo* and analyzed with the following result:

0.2818 gram substance gave, by the Carius method, 0.3116 gram AgBr.

	Calculated for $C_6HBr_2.NO_2(OCH_3)_2$.	Found.
Br	46.91	47.06

The same substance was formed also by boiling the anisol, $C_6HBr_3.NO_2.OCH_3$, with a methyl alcohol solution of sodic methylate.

Properties of the Dimethoxydibromnitrobenzol.—When crystallized from alcohol, it forms tufts of very slender, long, branching, white needles, which melt at 81°. It shows a tendency to turn brown on standing. It is freely soluble in alcohol, ether, benzol, chloroform, or acetone; slightly soluble in methyl alcohol, glacial acetic acid, or ligroin; essentially insoluble in water. Alcohol or ether is the best solvent for it. Our attempts to saponify this substance with sulphuric acid, or to reduce it with tin and hydrochloric acid, led to unpromising black tars.

Action of Cold Sodic Ethylate on 3,4,5-Tribrom-1,2-dinitrobenzol.

2,3,4-Tribrom-6-nitrophenetol, $C_6HBr_3.NO_2.OC_2H_5$. — Six grams of the 3,4,5-tribrom-1,2-dinitrobenzol were mixed with the sodic ethylate made from 0.8 gram of sodium and 45 cc. of absolute alcohol, and the mixture shaken at ordinary temperatures for about fifteen hours. The product, which was more highly colored than in the corresponding experiment with the methylate, was precipitated with water. The aqueous filtrate gave a strong test for a nitrite, a weaker test for a bromide, and contained a minute amount of some phenol. The precipitate, which was nearly white, was purified by recrystallization from alcohol, until it showed the constant melting-point 74°. The substance was deposited from its alcoholic solution as an oil, which solidified when touched with a crystal of the compound. The pure body was dried *in vacuo* and analyzed with the following results:

0.1988 gram substance gave, by the Carius method, 0.2755 gram AgBr.

	Calculated for $C_6HBr_3.NO_2.OC_2H_6$.	Found.
Br	59.40	58.95

Properties of the Tribromnitrophenetol.—It crystallizes from alcohol in little, white rosettes, which turn yellow, and afterward brown, on standing. It melts at 74°. It is freely soluble in ether, benzol, chloroform, or acetone; slightly soluble in alcohol, methyl alcohol, glacial acetic acid, or ligroin. We tried to saponify it by boiling it with sulphuric acid of sp. gr. 1.44, but obtained only dark decomposition-products, from which we did not succeed in isolating a definite compound.

When the action of the sodic ethylate on the 3,4,5-tribrom-1,2-dinitrobenzol was carried on at the boiling-point of alcohol, the product was a reddish tar of most unpromising appearance.

Action of an Aqueous Solution of Sodic Hydrate on 3,4,5-Tribrom-1,2-dinitrobenzol.

Ten grams of the 3,4,5-tribrom-1,2-dinitrobenzol were boiled in a flask with a return-condenser with 150 cc. of a 10 per cent solution of sodic hydrate prepared from sodium. The liquid turned dark-red almost immediately, and in a few hours began to deposit a bright crimson, crystalline precipitate. To make the reaction as complete as possible the boiling was continued for about fourteen hours, after which the liquid was allowed to cool and the precipitate filtered out. It was then washed through the filter with hot water in order to separate it from unaltered tribromdinitrobenzol. A portion of this filtrate was acidified with dilute nitric acid, the precipitate formed filtered out, and the filtrate tested for a nitrite with starch paste and potassic iodide, when a strong test was obtained. Another portion of the filtrate showed a mere trace of bromide with argentic nitrate. The main portion of the filtrate was acidified with hydrochloric acid, which threw down a yellow crystalline precipitate of the free phenol. The solution was kept cool during the acidification, as otherwise the precipitate showed a tendency to be tarry. The substance was also purified sometimes by precipitating at once with hydrochloric acid and removing the unaltered tribromdinitrobenzol with cold benzol, in which it is soluble, but the phenol nearly insoluble. This separation, however, is rather more tedious than that with boiling water. The crude phenol in either case was recrystallized from hot benzol until it showed the constant melting-point 120° to 121°, when it was dried and analyzed with the following results:

I. 0.2622 gram substance gave, by the Carius method, 0.3939 gram AgBr.

II. 0.2135 gram substance gave 0.3209 gram AgBr.

	Calculated for $C_6HBr_3.NO_2.OH$.	Found. I.	II.
Br	63.83	63.95	63.96

These analyses, in connection with those of its salts given later, show that the substance was formed by the replacement of one nitro group by a hydroxyl. Its constitution is probably $HO1.Br_32,3,4.NO_26$, and although this has not been proved experimentally, the arguments given in the introduction to this paper are so strongly in favor of this constitution that we shall call it provisionally the 2,3,4-tribrom-6-nitrophenol.

Properties of the 2,3,4-Tribrom-6-nitrophenol.—It crystallizes from hot benzol in rather thick, yellow prisms with square, or nearly square ends, and melts at 120° to 121°. It is freely soluble in chloroform, or acetone, or in hot benzol, but is nearly insoluble in cold benzol; soluble in alcohol, methyl alcohol, ether, or glacial acetic acid; slightly soluble in water or ligroin. The best solvent for it is hot benzol. Fuming nitric acid seems to destroy it completely. It dissolves easily in an aqueous solution of sodic hydrate with a bright-red color.

Sodium Salt of the 2,3,4-Tribrom-6-nitrophenol, $C_6HBr_3.NO_2.ONa$.—This substance was prepared by treating the pure phenol with sodic hydrate made from sodium and water, and purified by crystallization from hot water. It can also be prepared from the crude sodium salt, which is the direct product of the reaction, by washing it with cold water and then recrystallizing it from boiling water. After standing over night in a desiccator it was dried at 110°, when the loss amounted to less than 0.3 per cent, which showed that it was free from water of crystallization.

0.4018 gram salt yielded 0.0716 gram Na_2SO_4.

	Calculated for $C_6HBr_3.NO_2.ONa$.	Found.
Na	5.78	5.77

The salt forms bright crimson crystals, which are very slightly soluble in cold water, soluble in hot. It is more soluble in alcohol than in water. An aqueous solution of the salt gave a yellowish-orange precipitate with strontic nitrate, a brilliant reddish-orange precipitate with baric nitrate, and a red, flocculent precipitate with plumbic acetate.

Silver Salt of the 2,3,4-Tribrom-6-nitrophenol, $C_6HBr_3.NO_2.OAg$.—This substance was made by adding argentic nitrate to a solution of the sodium salt. The brilliant-red precipitate was washed with hot water and dried *in vacuo*.

0.4431 gram salt gave, when heated in a sealed tube with nitric acid, 0.1707 gram AgBr.

	Calculated for $C_6HBr_3.NO_2.OAg$.	Found.
Ag	22.37	22.13

It forms a brilliant red powder, essentially insoluble in cold water, but very slightly soluble in boiling water, from which it separates in small, red needles.

In order to connect this phenol with the anisol formed by the action of sodic methylate on the 3,4,5-tribrom-1,2-dinitrobenzol, we tried, as already stated, to saponify the anisol, and when this led to no satisfactory result we turned our attention to preparing the anisol from the silver salt of the phenol. For this purpose 0.5 gram of the salt was heated to 100° in a sealed tube with 10 cc. of methyl iodide, for six hours. The alcoholic extract of the product deposited crystals which, after purification by recrystallization, melted at 109° and crystallized in the characteristic form of the anisol. There can be no doubt, therefore, that the same nitro group is replaced by the hydroxyl and by the methoxyl group.

Sodic malonic ester acted on the 3,4,5-tribrom-1,2-dinitrobenzol in benzol solution, giving a red salt. On acidifying this a substance was obtained melting at 103° to 104°, which, according to a single determination of bromine, had the formula $C_6HBr_2(NO_2)_2CH(COOC_2H_5)_2$ (calculated 33.06, found 33.09), but as this is the only case observed by us in which an atom of bromine has been replaced in preference to a nitro group, we do not feel inclined to accept this formula until its correctness has been tested by additional experiments. Sodic acetoacetic ester also gave a similar red salt with the 3,4,5-tribrom-1,2-dinitrobenzol.

Action of Alcoholic Ammonia on 3,4,5-Tribrom-1,2-dinitrobenzol in the Cold.

2,3,4-Tribrom-6-nitraniline, $C_6HBr_3.NO_2.NH_2$.—Ten grams of the tribromdinitrobenzol were mixed with 150 cc. of an alcoholic solution of ammonia in an Erlenmeyer flask, and the mixture shaken for half an hour. A yellow, crystalline precipitate was formed in such quantity as to nearly fill the solution. It was allowed to stand over night to complete the reaction, after which it was poured into water and the yellow precipitate collected on a filter. The aqueous filtrate gave a strong test for a nitrite and a very faint one for a bromide. The washed precipitate was allowed to dry and then purified by recrystallization from benzol until it showed the constant melting-point 161°, when it was dried *in vacuo* and analyzed with the following result:

0.2486 gram substance gave, by the Carius method, 0.3754 gram AgBr.

	Calculated for $C_6HBr_3.NO_2.NH_2$.	Found.
Br	64.00	64.01

The substance has evidently been formed by the replacement of one nitro group by the amino group. It is an isomer of the tribromnitraniline, prepared, by Gallivan and one of us,[1] by the action of nitric acid on the 3,4,5-tribromacetanilide, since this substance melts at 130°. As this body, from the method of its preparation, must have the constitution NH_21, $Br_33,4,5.NO_22$, it follows that our compound melting at 161° must have the only other possible structure, $NH_21.Br_32,3,4.NO_26$. An attempt to convert the 2,3,4-tribrom-6-nitraniline into the corresponding phenol by the diazo reaction gave a product which showed a strong resemblance to the tribromnitrophenol, melting at 120° to 121°, described above. On account of a mistake in the work we cannot bring an absolute proof of the identity of these two bodies, and, unfortunately, this mistake was discovered so late that it could not be corrected without beginning the work from paranitraniline, which it is impossible for us to do at present. The structural formulas assigned to this phenol and its ethers are, therefore, not established by strict proof, although there is little doubt of their correctness.

Properties of the 2,3,4-Tribrom-6-nitraniline.—It crystallizes from benzol in bright-yellow, hair-like needles in radiating bunches, each made up of a few crystals. It melts at 161°. It is freely soluble in benzol, chloroform, or acetone; soluble in ether, methyl alcohol, or glacial acetic acid; slightly soluble in alcohol; and insoluble in cold ligroin or in water. In the hope of making a salt, some of the substance was dissolved in anhydrous benzol and treated with gaseous hydrochloric acid. No precipitate was formed, and the solution deposited the unaltered substance recognized by its melting-point, 161°.

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[1] This Journal, 20, 184 (1898).

A great many attempts were made to convert the substance into the corresponding nitrotetrabrombenzol as a step toward the preparation of the vicinal tetrabrombenzol, but our experiments in this direction led to no decisive results.

Action of Alcoholic Ammonia on 3,4,5-Tribrom-1,2-dinitrobenzol at 100°.

Dibromnitrophenylenediamine, $C_6HBr_2.NO_2(NH_2)_2$. — Two grams of the 3,4,5-tribrom-1,2-dinitrobenzol were heated to 100° in a sealed tube with 10 cc. of alcoholic ammonia for three days. At the end of this time the contents of the tube were washed into a beaker of water, when, upon standing, a yellow precipitate appeared, which was filtered out from the orange liquid. In the filtrate, both nitrite and bromide were found, and also the tribromnitrophenol melting at 120° to 121°. The precipitate was recrystallized from hot alcohol until it showed the constant melting-point 189° to 190°, when it was dried at 100° and analyzed with the following result:

0.0984 gram substance gave, by the Carius method, 0.1187 gram AgBr.

	Calculated for $C_6HBr_2.NO_2(NH_2)_2$.	Found.
Br	51.44	51.36

The substance is formed, therefore, by the replacement of 1 atom of bromine and one nitro group by two amino groups. The nitro group replaced is undoubtedly that lying between one atom of bromine and the second nitro group, as this was the one replaced by the amino group during the action of alcoholic ammonia in the cold. The bromine replaced would then be the atom para to the remaining nitro group, as no other is in a position to be replaced easily, if the tribromnitraniline is formed before the replacement of the bromine. This would give the substance the constitution $Br_2 2,4.NO_2 6.(NH_2)_2 1,3$. Some qualitative experiments confirmed this view of the structure of the diamine. A small quantity of it gave no blue color, when treated with hydrochloric acid, ferric chloride, and sulphuretted hydrogen. It would seem, therefore, that it is not a paradiamine. Another sample gave no action with a concentrated acetic acid solution of phenanthrenequinone, even when the mixture was warmed, which would indicate that it was not an orthodiamine. This leaves only the meta position for the two amino groups, which agrees with the conclusion arrived at on the general considerations stated above. We therefore adopt the name 2,4-dibrom-6-nitrometaphenylenediamine for this substance, but it should be remembered that this constitution does not rest on strict experimental proof, as the absence of the reaction for a para- or orthodiamine may have been due to the presence of the strongly negative radicals in the molecule, although this does not seem very probable.

Properties of the 2,4-Dibrom-6-nitrometaphenylenediamine.—It crystallizes in hour-glass-shaped bunches of branching needles, which have a bright-yellow color and melt at 189° to 190°. It is very freely soluble in acetone ; soluble in alcohol, methyl alcohol, ether, chloroform, or glacial acetic acid ; slightly soluble in benzol ; very slightly soluble in ligroin ; essentially insoluble in water. The best solvent for it is hot alcohol. It forms no chloride, even when a solution of it in benzol is saturated with gaseous hydrochloric acid.

Action of Aniline on the 3,4,5-Tribrom-1,2-dinitrobenzol.

2,3,4-Tribrom-6-nitrodiphenylamine, $C_6HBr_3.NO_2.NHC_6H_5$.—Half a gram of the 3,4,5-tribrom-1,2-dinitrobenzol was boiled with a few cubic centimeters of aniline, in a test-tube, for about a minute. After it had cooled the solution was poured into water and the excess of aniline removed with dilute hydrochloric acid. The reddish-brown product, after being washed with dilute hydrochloric acid and water, was recrystallized from alcohol until it showed the constant melting-point 138° to 139°, when it was dried and analyzed with the following result :

0.2173 gram substance gave, by the Carius method, 0.2726 gram AgBr.

	Calculated for $C_6HBr_3.NO_2.NHC_6H_5$.	Found.
Br	53.21	53.38

Properties.—When first crystallized from alcohol it gave a mixture of short, bright-red prisms and rosettes of long, delicate, yellow needles, but after several crystallizations from alcohol it was converted entirely into the red prisms. It seems probable from this observation that it occurs in two modifications, as this is not unusual in related aniline bodies.[1] It melts at 138° to 139°. It is soluble in ether, benzol, chloroform, or acetone; slightly soluble in alcohol, methyl alcohol, or glacial acetic acid; insoluble in ligroin or water. The best solvent for it is alcohol.

Reduction of 3,4,5-Tribrom-1,2-dinitrobenzol.

3,4,5-Tribromorthophenylenediamine, $C_6HBr_3(NH_2)_2$.

Twenty grams of the 3,4,5-tribrom-1,2-dinitrobenzol were warmed on the steam-bath in an Erlenmeyer flask with tin and strong hydrochloric acid for a day. The grayish residue was filtered out, boiled with a small quantity of aqueous sodic hydrate to remove hydrates of tin, and this filtered off while nearly boiling. The diamine was then extracted from the insoluble part with acetone, leaving the metallic tin. The residue, after evaporating off the acetone, was purified by crystallization from alcohol and analyzed with the following result:

0.1600 gram substance gave, by the Carius method, 0.2610 gram AgBr.

	Calculated for $C_6HBr_3(NH_2)_2$.	Found.
Br	69.56	69.42

This analysis was confirmed by one of the chloride made by dissolving the diamine in benzol, saturating with gaseous hydrochloric acid, and washing the precipitate with benzol, when it was dried *in vacuo* and analyzed.

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[1] This JOURNAL, **14**, 348; **16**, 35; **26**, 5.

0.1686 gram substance gave, by the Carius method, 0.3107 gram AgBr and AgCl.

	Calculated for $C_6HBr_3.NH_2.NH_3Cl$.	Found.
Br + Cl	72.21	71.76

The melting-point observed by us was 91°, but owing to the ease with which the diamine turned brown in the air we do not feel certain that it is exact. It is freely soluble in ether or acetone; soluble in alcohol, methyl alcohol, benzol, or glacial acetic acid; slightly soluble in chloroform; essentially insoluble in ligroin or water. With hydrochloric acid it gives the salt $C_6HBr_3.NH_2.NH_3Cl$, as already mentioned.

Diphenylene-3,4,5-tribromquinoxaline, $C_6HBr_3N_2C_2C_{12}H_8$. — Two grams of the diamine just described, dissolved in about 30 cc. of alcohol, were mixed with 1.2 grams of phenanthrenequinone, dissolved in somewhat more than 125 cc. of glacial acetic acid. The mixture nearly solidified, and after standing half an hour the precipitate was sucked dry on the pump, extracted several times with a mixture of acetone and very little benzol, pressed on a porous plate, and dried in a desiccator containing calcic hydrate and chloride.

0.2368 gram substance gave, by the Carius method, 0.2602 gram AgBr.

	Calculated for $C_6HBr_3N_2C_{14}H_8$.	Found.
Br	46.40	46.77

It formed a yellow solid, which did not melt even at 250°, and was essentially insoluble in all solvents.

Diphenyl-3,4,5-tribromquinoxaline, $C_6HBr_3N_2C_2(C_6H_5)_2$. — Two grams of the orthodiamine dissolved in alcohol were mixed with 1.2 grams of benzil dissolved in glacial acetic acid. At first there was no action, but after adding a few crystals of benzil a brown precipitate began to form, which was deposited in considerable quantity after the mixture had stood over night. It was purified by washing with a small quantity of alcohol and dried in a desiccator over calcic chloride and lime.

0.2153 gram substance gave, by the Carius method, 0.2345 gram AgBr.

	Calculated for $C_6HBr_3.N_2C_2(C_6H_5)_2$.	Found.
Br	46.24	46.34

It forms a light, brick-red powder, freely soluble in benzol or chloroform ; soluble in ether or acetone ; slightly soluble in alcohol, methyl alcohol, or glacial acetic acid ; essentially insoluble in ligroin or water.

OBITUARY.

HENRY BARKER HILL.

The death of Henry Barker Hill, on April 6, 1903, left a gap in the ranks of American chemists which will not be easily filled. Born at Waltham, April 27, 1849, he grew up in a scholarly atmosphere, as he was the son of the Rev. Thomas Hill, president of Antioch College, and later of Harvard University. After graduating from Harvard College, in the class of 1869, he spent a year in Berlin, studying chemistry under A. W. Hofmann, and in 1870 accepted a position in Harvard University, where he served for the following thirty years as Assistant, Assistant Professor, Professor, and Director of the Laboratory.

He took up his duties in Cambridge with only a meagre equipment as a chemist and an enthusiastic determination to make a place for himself in chemical research, but the necessary training came slowly, as he was without a teacher and hampered by the onerous duties of his position, so that his first paper was not published till 1876. This paper, however, showed none of the crudeness and uncertainty of touch usually characteristic of first papers, but seemed rather the work of a mature finished chemist. In it he described methyluric acid, and by following the fate of the methyl group in its decomposition-products succeeded in throwing much light on the constitution of uric acid.

His attention, however, was soon diverted from this line of work, promising as it was, by his discovery of furfurol among the waste products of the manufacture of acetic acid by heating wood at comparatively low temperatures, and the exploration of the almost unknown field thus opened kept him busy till the end of his life. His work on the furfurane group is described in over thirty papers, and among his most striking achievements may be noted the full study of mucobromic and mucochloric acids with the determination of their puzzling constitution, and the investigation of numerous substituted propionic, acrylic, and propiolic acids derived from them; the description of the brom- and chlorpyromucic acids, in which the interesting fact was brought out that these two halogens differ in their behavior with pyromucic acid; the discovery of nitromalonic aldehyde, and a long line of brilliant aromatic syntheses from it; a study of methylfurfurol, found in the fractions boiling above furfurol, and of its most important derivatives. At the time of his death he was investigating pyrazol compounds from the oxime of nitromalonic aldehyde, and the reduction-products of dehydromucic acid, some of which he had succeeded in separating into the optically active forms.

His work has converted the furfurane group from one of the least known to one of the most perfectly explored domains of chemistry—a monument of which any chemist may feel proud.

An examination of these papers brings out Hill's great qualities as a chemist—his grasp of the subject and power of close and logical reasoning, his uncommon experimental ability, and above all the thoroughness and accuracy which were his most striking and peculiar characteristics. These were the expression of his almost passionate devotion to truth. Most chemists are content to accept the work of their students after testing it in two or three places, but he was never willing to publish until he had repeated the whole of it with his own hands, and if this diminished the number of his papers, it gave them a finish and authority rarely, if ever, found in those of others.

In his teaching the same thoroughness and accuracy were conspicuous. No one ever heard an incorrect statement in his lectures, which were models of comprehensiveness and preservation of the just relation between the important and the unimportant. In his course in investigation the rigorous thoroughness of his work repelled many students, but this did not displease him, as he always preferred quality to quantity.

This is not the place to dwell on his wonderful executive ability, which converted an antiquated building, planned for 40 students, into an adequate laboratory for 700, and organized the varied business of this large department so that it runs smoothly even now, when deprived of its chief. But attention should be called to the new forms of apparatus with which he has enriched the laboratories at Cambridge—the unique hoods and water-baths for the public rooms, and his many devices for research work, some of which will soon be described in this JOURNAL.

His overflowing energy was not confined to his profession. His reading was wide and judicious in the literatures of more than one language, and he was a genealogist and a musician of no mean attainments.

In this brief note I have tried to show Hill as he was, a man of wide interests and of many and varied excellencies, an admirable teacher, a business man of marked ability, an ingenious inventor, a great chemist, and above all a lover of truth. C. L. J.

REVIEWS.

EINFÜHRUNG IN DIE ELEKTROCHEMIE, NACH DER ELEKTROLYTISCHEN DISSOCIATIONSTHEORIE. Bearbeitet von PETER GERDES. Mit 48 in den Text gedruckten Abbildungen. Druck und Verlag von Wilhelm Knapp. Halle, a. S. 1902. pp. 123.

The ground covered by this little book can be seen from the table of contents. A discussion of electrical units is followed by an account of osmotic pressure, which omits the all-important work of Morse in this field. Chapter III treats of electrolysis and II of polarization. The subject of the neutralization of acids and bases is followed by a brief and fairly satisfactory description of a number of the most common forms of primary cells, including the Daniell, Bunsen, Leclanché, and bichromate batteries. This is followed by a brief account of the electrolytic deposition of the metals.

The book will undoubtedly be found useful by those who have not the time nor inclination to read some larger work on physical chemistry. H. C. J.

ASSAYING AND METALLURGICAL ANALYSIS FOR THE USE OF STUDENTS, CHEMISTS, AND ASSAYERS. By E. L. RHEAD, Lecturer on Metallurgy, Municipal School of Technology, Manchester, and A. HUMBOLDT SEXTON, F.S.C., F.C.S., Professor of Metallurgy, Glasgow, and West of Scotland Technical College. London: Longmans, Green & Co. 1902.

This beautifully printed and illustrated book is written as a comprehensive handbook, to include all the work likely to be required in the laboratory or assay office. It is too large and too varied in contents to supplant the smaller manuals of assaying or of analysis, but it covers the entire field.

Part I., 52 pages, describes laboratory apparatus and general methods. In Part II., 236 pages, under the name of each metal, a complete description of compounds, reactions, and analytic methods is given. For example, under the heading Bismuth, the ores and alloys are described, as are the chemical reactions by tests in the dry way and in solution; the dry assay, (*a*) of ores free of sulphur, (*b*) of sulphurized ores free of copper, (*c*) of ores with copper present; refining; the wet assay; gravimetric methods, including estimation as oxide, as metal, by precipitation as sulphide; treatment of antimonial and arsenical ores; electrolytic assay; volumetric methods; Abel and Fields' method for the determination of bismuth in copper.

Part III., 108 pages, gives examples of metallurgical analysis. This part also is very satisfactory, and avoids repetition by copious cross-references in the text. As an example taken at random, under the heading Silicon in Iron and Steel, the following methods are well treated: 1. Estimation of silicon by solution of the metal in acid and weighing as silica; 2. Drown's sulphuric acid method; 3. Allen's method; 4. Estimation by iodine; 5. By chlorine.

The book is indeed a comprehensive laboratory handbook, and as such should be welcomed in all laboratories, particularly in those for technical and commercial work. E. R.

GUIDE TO PREPARATION WORK IN INORGANIC CHEMISTRY FOR STUDENTS OF CHEMISTRY AND PHARMACY. By DR. REINHART BLOCHMANN, Professor at the University of Königsberg, with numerous illustrations. Authorized translation by JAMES LEWIS HOWE, Washington and Lee University. Published by the Department of Chemistry, Washington and Lee University, Lexington, Virginia. pp. 65. Price, 60 cents.

The first German edition of Blochmann's book was published in 1895. A review of it appeared in the same year in this JOURNAL,[1] in which it was favorably mentioned.

Few teachers of chemistry pay enough attention to inorganic preparations. No other elementary work interests students so much. If a beginner in the laboratory, who has worked a little ahead of his class, is allowed to fill up extra time by making one or two preparations with due care, the stimulus that "making" something gives him will be felt in his attitude toward his later work.

Professor Blochmann uses inexpensive material and ingeniously utilizes the product or by-product of one preparation as material for others.

Professor Howe has used this book for several years in his own classes, and has made an excellent translation from a copy specially corrected and annotated by the author. It is to be hoped that as this excellent little manual is now obtain-

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[1] This JOURNAL, 17, 544.

able in English translation at a low price it may come into frequent use.
E. R.

A COURSE IN QUALITATIVE CHEMICAL ANALYSIS. By F. P. VENABLE, PH.D., F.C.S., Professor of Chemistry in the University of North Carolina. Revised by ALVIN S. WHEELER, A.M., PH.D., Associate Professor of Chemistry in the University of North Carolina. Fourth edition. New York: University Publishing Co. 1902.

Professor Venable's little book, while very brief and simple, gives careful directions for work and clear explanations of the various reactions. It may be commended to those who prefer a short manual.

THE GENERAL PRINCIPLES OF PHYSICAL SCIENCE: AN INTRODUCTION TO THE STUDY OF THE GENERAL PRINCIPLES OF CHEMISTRY. By ARTHUR A. NOYES, Professor of Theoretical Chemistry in the Massachusetts Institute of Technology. New York: Henry Holt & Co. 1902. pp. 172.

The work in hand is not a complete treatise but simply the introduction to a large work on the general subject of theoretical chemistry. In the author's words: "It forms the first introductory part of a projected work upon this science to be entitled 'The General Principles of Chemistry,' the latter parts of which are to treat in succession of the general theories of chemistry, of the relations between physical properties and chemical composition, of the principles relating to the occurrence and equilibrium of chemical changes, and of the principles relating to the energy changes attending chemical changes."

The introduction deals with the object, the methods, and the subdivisions of science, the fundamental concepts of physical science, the general principles relating to matter, and the general principles relating to energy.

It is obvious that this but paves the way for the general discussion of theoretical or physical chemistry. The style is unusually clear and concise, and the work as a whole will be a valuable contribution to physical chemical literature.
H. C. J.

LEHRBUCH DER ALLGEMEINEN CHEMIE. Von DR. WILHELM OSTWALD, Professor an der Universität zu Leipzig. In zwei Bänden. Zweite umgearbeitete Auflage; zweiten Bandes, zweiter Teil; Verwandtschaftslehre, erster Teil, mit 389 Textfiguren. Verlag von Wilhelm Engelmann. 1896–1902. pp. 829–1188.

The conclusion of the second part of the second volume of Ostwald's Lehrbuch will be welcomed by all, and especially by those who possess the earlier portions of this great handbook on physical chemistry. The number in hand treats of the subject of chemical equilibrium of the second order, and then takes up and completes the discussion of chemical equilibrium of the third order.

The second edition of the "Lehrbuch" is, however, not yet completed. The second part of the second volume is to be followed by a third part, which will treat of solid solutions, isomorphous mixtures, enantiomorphous crystals, electrochemical equilibrium, catalysis, dissociation and equilibrium constants, etc. This will then be followed by a supplement, which will deal systematically with the work which has been published during the appearance of the various parts of the second edition.

With this will end the gigantic task which Ostwald has imposed upon himself, and for which physical chemistry in all time will owe a deep and lasting debt of gratitude.

H. C. J.

LA CIDRERIE MODERNE OU L'ART DE FAIRE LE BON CIDRE. Par GEORGES JACQUEMIN, Directeur scientifique de l'Institut La Claire, et HENRI ALLIOT, Ingénieur agricole. Malzéville-Nancy: Imprimerie Edg. Thomas. 1902. pp. 712. Price, 10 fr.

The authors, who conduct a research laboratory for the study of agricultural chemistry and related subjects, have undertaken to publish a series of monographs under the general title: "La Technologie agricole moderne." The book before us is the first of these. The subject is treated with thoroughness from different points of view. There are chapters on the history of cider, its hygienic effects, and statistics. The structure and composition of apples and pears, the methods of propagating from seed, the different ways of grafting, and the most approved cultural methods of pears and apples are given, as well as an account of their diseases. Then follow chapters on the care of the fruit and machinery, the extraction of the juice, the ferments of cider, the best methods of fermentation and preservation of cider and perry. The diseases of cider and their treatment, the manufacture of alcohol and vinegar, and the preparation of dried apples and pears are also discussed. On the whole, the book will be of value to any one engaged in this business. There are numerous illustrations.

C. E. W.

DIE BESCHÄDIGUNG DER VEGETATION DURCH RAUCH: HANDBUCH ZUR ERKENNUNG UND BEURTEILUNG VON RAUCHSCHÄDEN. By E. HASELHOFF, Director of the Agricultural Experiment Station in Marburg a. d. Lahn, and G. LINDAU, Privatdocent in Botany and Curator of the Royal Botanical Museum in Berlin. Berlin: Gebrüder Borntraeger. 1903. pp. 412. 27 illustrations.

This interesting book is a study of one of the most important and annoying problems with which the forester and agriculturist has to deal. It has long been recognized that smoke affects vegetation injuriously, and many observers have investigated the question, both in the field and in the laboratory. This book gives an account of much of this work, in which the authors had a share, and shows, as far as possible, just what part is played by the different constituents of smoke from dwellings, factories, acid works, and metallurgical furnaces. The greatest injury is not caused by the solids (soot, etc.) in the smoke but by the gases, among which sulphur dioxide is the most harmful, especially as it is produced nearly always when fuel is burned. It has been estimated that the various factories in St. Helens, England, send into the air 36,108,000 kilograms of sulphur in the form of sulphur dioxide, etc., each year. Most of this comes from the coal. Besides this, the effects of chlorine, hydrochloric acid, hydrofluoric acid, nitric acid, acetic acid, ammonia, hydrogen sulphide, bromine, asphalt, illuminating gas, pyridine, phenol, flue dust, etc., have been investigated. The specific action of the different poisons and the means of distinguishing between the injuries caused by them and insects, etc., are described as far as possible.

The physiological and structural changes in the leaves, the injury done to vegetables and forest trees, and the relative power of resistance of different species of trees are all studied. The injury caused by a given factory extends over an ellipse with its long axis in the direction of the prevailing wind, and with the factory at one of the foci ; that is, the harm done is greatest to leeward. Evergreens, such as pine, spruce, and larch, suffer more than deciduous trees, which practically escape the action of the smoke for a part of the year, during which time they have a chance to recuperate.

The book is of great interest, not only to those for whom it was written, but also to the chemist and botanist.

C. E. W.

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CYANOGEN IODIDE AS AN INDICATOR FOR ACIDS.

BY J. H. KASTLE AND MARY E. CLARK.

It has been pointed out by E. von Meyer[1] that cyanogen iodide and hydriodic acid react to form hydrocyanic acid and iodine, thus:

$$HI + ICN = HCN + I_2.$$

This reaction seems to be a general one for iodides under proper conditions. We have found, for example, that cyanogen iodide also decomposes potassium iodide even in tolerably dilute solutions, and that it acts on mercuric iodide when the latter is suspended in water. It also liberates large amounts of iodine from ethyl iodide at 150° C. With the metallic iodides this reaction has been found to depend largely on the concentration. On normal solutions of potassium iodide, cyanogen iodide has been found to act at once in the cold with the liberation of iodine. This may be shown by bringing together 1 cc. of N-potassium iodide, 1 cc. of N/100 cyanogen iodide, and a small amount of starch paste. The solution becomes dark blue at once. On the other hand, if N/100 potassium iodide and N/100 cyanogen iodide be brought together in the presence of starch no iodide of starch is produced. If, however, to this colorless mixture a drop of acid be added, the solution becomes blue at once, indicating that cyanogen iodide acts upon hydriodic acid much more readily than it does upon potassium iodide. Indeed the reaction is one of extreme delicacy. It occurred to us, therefore, that it might not be without interest to determine the quantities of various acids required to effect the reaction in question. In order to do this, however, it was first necessary to test the conduct of cyanogen iodide towards potassium iodide at different concentrations. In all of our experiments a N/100 solution of cyanogen iodide in water was employed. The conduct of this solution towards potassium iodide was tested by bringing together 1 cc. N/100 cyanogen iodide, 1 cc. of potassium iodide of given concentration, and 1 cc. of a clear solution of starch containing 0.1 gram of starch in 100 cc. of water. The results of these observations are given in Table I. :

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[1] J. prakt. Chem., 36, 292, 299.

Table I.

Dilution of potassium iodide.	Color of the mixed solution.
N	Deep blue, immediately
N/2	" " "
N/8	" " not instantaneous
N/10	" " " "
N/20	Lighter blue, not "
N/50	Light blue, after standing some time
N/100	Colorless, even after standing some time

It has been found that small amounts of impurities greatly affect the results. Absolute cleanliness of apparatus is necessary in carrying out the tests if concordant results are to be obtained. The minutest trace of acids in the apparatus or reagents may often vitiate an entire series of experiments. It will be observed that the limit of the reaction of cyanogen iodide on potassium iodide is reached at a concentration not exceeding N/100 for each. Hence the mixture of N/100 cyanogen iodide, N/100 potassium iodide, and 0.1 per cent starch solution in equal proportions by volume furnished us with a reagent upon which to test the conduct of different acids.

The tests upon acids were conducted in the following manner: To 1 cc. of the acid to be tested there was added, in the order named, 1 cc. N/100 potassium iodide, 1 cc. 0.1 per cent starch solution, and 1 cc. N/100 cyanogen iodide. In order to make more certain of the results, control experiments were carried out at intervals, using 1 cc. of water in place of the acid, the other substances remaining the same. The following acids were employed in the experiments, *viz.*, hydrochloric, sulphuric, benzenesulphonic, *p*-nitrotoluenesulphonic, oxalic, butyric, and carbonic. The results of these tests for all the acids, except carbonic and sulphuric, are given in Tables II. and III.

Table II.

Name of acid.	Dilution.	Color of the mixed solution.
Hydrochloric	N/1000	Dark blue
"	N/4000	Very light blue
"	N/5000	Colorless
p-Nitrotoluenesulphonic	N/1000	Dark blue
"	N/4000	Very light blue
Benzenesulphonic	N/1000	Dark blue
"	N/5000	Colorless
Oxalic	N/1000	Dark blue
"	N/5000	Colorless
Butyric	N/1000	Dark blue
"	N/2000	" "
"	N/3000	Light blue
"	N/4000	Colorless

Similar experiments were tried, using N/50 instead of N/100 potassium iodide.[1] The results are given in Table III.:

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[1] While N/50 potassium iodide has been found to react with the cyanogen iodide alone, it is nevertheless possible to employ it of this strength in testing for acids by this method, if the tests are properly controlled by experiments in which water is employed instead of the acid being tested. With water and potassium iodide of this dilution the blue color develops only slowly. With dilute acids iodide of starch is formed immediately.

Table III.

Name of acid.	Dilution.	Color of the mixed solution.
Hydrochloric	N/4000	Distinct blue
"	N/5000	" "
"	N/10,000	Colorless
"	N/50,000	"
p-Nitrotoluenesulphonic	N/4000	Distinct blue
"	N/5000	" "
"	N/10,000	Colorless
Benzenesulphonic	N/5000	Distinct blue
"	N/10,000	Light blue
Oxalic	N/5000	Distinct blue
"	N/10,000	Colorless
Butyric	N/4000	Distinct blue
"	N/5000	Colorless

It has been observed that the sensitiveness of the reagent depends a great deal on the purity of the cyanogen iodide. The compound employed in our experiments was prepared by two entirely different methods, *viz.*, by the action of iodine on mercuric cyanide in ether solution, and by subliming a mixture of potassium cyanide and iodine. While both specimens of the compound were purified by sublimation it was still found that the compound prepared by the latter method was more sensitive towards acids. With the compound prepared from mercuric cyanide the limit of the reaction, for most acids at least, was N/5000, whereas with the compound prepared from potassium iodide and iodine the limit of the reaction was reached only with N/10,000 acid.

At present we are unable to explain this difference in conduct on the part of the cyanogen iodide prepared by these two methods. Regardless of this, however, it has been found possible to recognize any one of the above-named acids, with the exception of carbonic, at a dilution of 1 gram molecular weight of the acid in 20,000 to 40,000 liters of water, taking into consideration, of course, the fact that an acid of any degree of dilution was further diluted four times when added to the reagent. Expressed somewhat differently, these acids have been recognized by means of this reagent in the following quantities:

Acid.	Parts per million.
Hydrochloric	1.8
Benzenesulphonic	7.9
p-Nitrotoluenesulphonic	10.85
Oxalic	3.15
Butyric	5.5

Or by means of the more sensitive reagent :

Sulphuric	1.225
Benzenesulphonic	3.95
Oxalic	1.56

Some idea of the delicacy of cyanogen iodide as a reagent for acids may be formed by a comparison with other indicators. The following data are taken from Trommsdorf's table,[1] showing the sensitiveness of the more common indicators towards acids :

Indicator.	Strength of indicator.	Volume of titrated fluid. cc.	Volume of acid required.	Parts per million of acid required. cc.
Azolitmin	1 : 100	100	1.2 cc. N/100 HCl	4.38
Cochineal	1 : 80	“	3.0 “ “ “	10.95
Congo red	1 : 100	“	0.7 “ “ “	2.55
Corallin	1 : 100	“	0.6 “ “ “	2.19
Fluorescein	1 : 100	“	0.5 “ N/10 “	18.25
Litmus	1 : 10	“	0.05 cc. “ “	1.82
Methyl orange	1 : 200	“	1.0 “ N/100 “	3.65
Phenolphthalein	1 : 100	“	0.5 “ “ “	1.82
Rosolic acid	1 : 100	“	0.7 “ “ “	2.55

It will be observed, therefore, that by means of cyanogen iodide it is possible to recognize the same quantity of hydrochloric acid that can be detected by litmus and phenolphthalein. In fact, in the case of sulphuric, benzenesulphonic, and oxalic acids we have been able to recognize a quantity of acid equivalent to one-half of this amount of hydrochloric acid.

From the results thus far reached it would seem that the delicacy of the reaction is in no wise dependent on the affinity of the acid. At least such is the case for the dilutions at which we have worked thus far. The limit of the reaction for the strong acids, such as hydrochloric, sulphuric, benzenesulphonic, and *p*-nitrotoluenesulphonic, is nearly, if not quite, the same as for the weaker acids, oxalic and butyric.

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[1] Indicators and Test-papers, Cohn, pp. 220–222.

Some idea of the delicacy of the reaction under consideration is also afforded by the conduct of the reagent towards carbonic acid. As is well known, the conduct of this acid towards most indicators is very uncertain. With the mixture containing equal amounts by volume of N/100 cyanogen iodide, N/100 potassium iodide, and 0.1 per cent starch solution we have obtained the following results with this acid :

Dilution.	Color of the mixed solution.
N/2	Dark blue
N/3	Blue
N/100	Distinct blue

It will be observed, therefore, that by means of this reagent we have been able to recognize the presence of 77 parts of carbonic acid per million, and in all probability this is by no means the limit of the reaction for this acid. Whether a very weak acid like carbonic will give the reaction at the very great dilutions at which it has been obtained with hydrochloric and other strong acids remains to be seen.

Cyanogen Iodide as a Reagent for Measuring the Hydrolysis of Salts.

In view of the ease with which very small amounts of acids can be recognized by means of cyanogen iodide, it occurred to us to test the conduct of the compound towards various salts, particularly towards those that were known to be hydrolyzed in aqueous solution. The tests were conducted after the manner already described for acids, *i. e.*, to 1 cc. of the given salt, at known dilution, there was added, in the order named, 1 cc. of N/100 potassium iodide, 1 cc. of 0.1 per cent starch solution, and 1 cc. of N/100 cyanogen iodide. The formation of the iodide of starch indicated the presence of free acid in the solution of the salt. The names of the salts that have thus far been tested, together with the dilutions at which they were employed, and all other data, are given in Table IV., in which are also to be found the results of these experiments :

Table IV.

Name of salt.	Dilution.	Color produced.	Time of reaction.
Alum	N/10	Dark blue	Instantly
Potassium sulphate	"	Colorless	10 minutes
Potassium nitrate	"	"	30 "
Zinc sulphate	"	Faint blue	30 "
Magnesium sulphate	"	Colorless	1 hour
Ammonium sulphate	"	"	1 "
Aluminium chloride	"	Dark blue	Immediately
Manganese sulphate	"	Faint blue	" (increasing slowly on standing)
Potassium chloride	"	"	Immediately (increasing slowly on standing)
Chrome alum	"	Dark blue	Immediately
Aluminium nitrate	"	"	1 minute
Cadmium chloride	"	Colorless	30 minutes
Ferrous sulphate	"	Dark blue	Immediately
Ammonium ferric sulphate	"	"	"
Ferric nitrate	"	"	"
Nickel sulphate	"	"	Gradually
Nickel ammonium sulphate	"	Light blue	"
Nickel potassium sulphate	"	"	"
Nickel nitrate	"	"	"
Cobalt nitrate	"	Colorless	After 3 hours
Cobalt ammonium sulphate	"	"	Immediately (on long standing it became blue)
Cobalt potassium sulphate	"	Light blue	Gradually

In order to determine whether any one of these salts brought about the formation of the iodide of starch as the result of oxidation, control experiments were tried in doubtful cases, in which 1 cc. of water was used instead of the N/100 cyanogen iodide, the other substances remaining the same. It was found as the result of these trials that the iodide of starch was formed with the following salts, *viz.*, ferric nitrate and ferric sulphate. Even with these salts, however, the production of the iodide of starch is much slower when acting alone than in the presence of the cyanogen iodide, so that the hydrolysis of these salts in aqueous solution is indicated just as certainly as in the case of those that do not cause the formation of the iodide of starch by oxidation.

It is apparent from these results that such neutral salts as potassium nitrate, potassium sulphate, magnesium sulphate, and ammonium sulphate are not hydrolyzed in their aqueous solution. On the other hand, potassium chloride gave a blue color with the reagent. This exceptional conduct on the part of this neutral salt is probably to be accounted for by the supposition that cyanogen iodide reacts directly with potassium chloride with the production of cyanogen chloride and potassium iodide. This last would then react with any excess of cyanogen iodide remaining in the manner already indicated above.

According to the indications afforded by the new reagent, aluminium, chromic, ferrous, and ferric salts are hydrolyzed to a greater degree than those of any other metal or basic radical. Salts of nickel, cobalt, manganese, and zinc are hydrolyzed to a much less extent, and cadmium chloride not at all.

This last result is at variance with the results reached by Long[1] in his investigation of the inversion of cane sugar by salts. According to Long, cadmium chloride inverted cane sugar more rapidly than any other salt employed in his experiments. At present we are unable to account for this peculiar difference in the conduct on the part of cadmium chloride.

In view of the ease with which very small amounts of free acid may be recognized by means of cyanogen iodide, it occurred to us that possibly the reagent might be employed to measure the amount of hydrolysis of hydrolyzable salts. The attempt has been made, therefore, to determine the extent to which potassium alum is hydrolyzed at great dilution. This was done by comparing the color produced with 1 cc. of alum solution of known concentration with that produced by a known quantity of sulphuric acid. Two solutions were prepared, one containing one molecular weight in grams of alum in 100 liters of water, the other one-half of one molecular weight in grams of sulphuric acid. The dilution of the solution of alum may therefore be denoted by M/100, and that of the sulphuric acid by N/100 $(H_2SO_4)_{\frac{1}{2}}$. The acid was therefore equivalent to N/100 hydrochloric, and for equal volumes of solution was equivalent to one-sixth of the sulphuric acid contained in the alum as aluminium sulphate. These two solutions were employed as the basis for subsequent dilutions. The conduct of these very dilute solutions of alum and sulphuric acid was then tested towards the reagent (N/100 cyanogen iodide, N/100 potassium iodide, and 0.1 per cent starch paste) in the manner already described above. In the following table are given the results of this comparison :

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[1] J. Am. Chem. Soc., 18, 717.

Alum.			*Sulphuric acid.*	
Dilution.	Color produced with reagent.	A.	Color produced with reagent.	Dilution.
M/10,000	Dark blue	>	Light blue	N/10,000 $(H_2SO_4)_{\frac{1}{2}}$
M/20,000	Blue	>	"	" "
M/30,000	"	>	"	" "
M/40,000	"	>	"	" "
M/50,000	Light blue	=	"	" "
M/60,000	"	<	"	" "
M/70,000	"	<	"	" "

In column A of the above table the sign of greater or less and the sign of equality are used to indicate that the amount of iodide of starch produced by the alum at the given dilution is greater or less than, or equal to, that produced by the sulphuric acid. It is evident from these results that when acting on a mixture of 1 cc. N/100 cyanogen iodide, 1 cc. N/100 potassium iodide, and 1 cc. 0.1 per cent starch, 1 cc. of M/50,000 alum produces the same quantity of iodide of starch as 1 cc. of N/10,000 $(H_2SO_4)_{\frac{1}{2}}$. On another occasion, using different solutions, it was found that M/60,000 alum was equivalent to N/10,000 $(H_2SO_4)_{\frac{1}{2}}$. Hence it follows that at a dilution of 200,000 to 240,000 liters the hydrolysis of alum amounts to from 83 to 100 per cent. Unfortunately, but few, if any, measurements of the hydrolysis of salts at such great dilutions have ever been made, so that at present we have no reliable data with which to compare our own results. It follows from the law of mass action, however, that if the hydrolysis of any salt is small it will increase very nearly proportionately to the square root of the dilution. Now, according to Long, 1.44 per cent of alum is hydrolyzed in the N/4 solution of this salt. If, therefore, the law of dilution held strictly for this salt at all concentrations, we would expect alum to be completely hydrolyzed at a dilution of 20,000 liters. Our results, therefore, would seem to be in harmony with the general theory of such processes. It should be borne in mind, however, that the chemical changes taken advantage of in the use of cyanogen iodide as an indicator are after all not as simple as they appear at first sight. Whether any of them are of such a nature as to introduce a disturbing factor into the equilibrium of the hydrolysis can only be determined by further investigation.

STATE COLLEGE OF KENTUCKY,
LEXINGTON, February, 1903.

A METHOD FOR CALIBRATING BURETTES.

BY D. W. HORN AND ELIZABETH M. VAN WAGENER.

The following method of calibrating burettes requires no special form of apparatus. It has proven satisfactory for the usual volumetric work of students, and is sufficiently accurate for more exact work.

An arrangement of apparatus similar to that in the Hempel gas-burette or Lunge nitrometer is used. Two burettes are mounted in an upright position on a tall iron stand and their tips are joined by a piece of rubber tubing. One of them is clamped firmly while the other can be raised or lowered, at the same time being guided by clamps fastened at different points along the upright rod of the stand. The calibration of one of them in terms of the other is accomplished by keeping the one stationary and causing water to flow into it from the other and movable one, which is gradually raised. The calibration is duplicated by lowering the latter again and causing the water to flow back into it.

The relative calibration thus obtained can be converted into an "absolute" one, provided one of the two burettes is calibrated by weighing the water it delivers between selected marks along its scale.[1] A burette thus standardized may be used in all subsequent calibrations as the standard with which other burettes may be compared by the arrangement of apparatus and the method already described.

In testing this method relative calibrations have been carried out under a variety of conditions. Burettes of the Mohr and Schellbach type have been used, readings have been made with and without floats, and soft rubber tubing in different lengths, both red and black, has been tried. In some cases the complete experiment was made by one of us. In others, after a calibration had been made by one, the duplicate calibration was made by the other. Sometimes only duplicates were made and at others the same calibration was repeated four or five times in succession. The records of some of these experiments are given in the following tables:

Number of reading.	Readings on stationary burette.	Readings on other burette, first series.	Readings on other burette, duplicate series.
1	50.00	0.00	0.00
2	48.00	2.00	2.00
3	46.00	4.00	4.00
4	44.00	6.00	6.00
5	42.00	8.01	8.00
6	40.00	10.04	10.04
7	38.00	12.02	12.02
8	36.00	14.03	14.03
9	34.00	16.01	16.01
10	32.00	18.00	18.00
11	30.00	20.00	20.00
12	28.00	21.99	21.99
13	26.00	23.98	23.98
14	24.00	25.99	25.99
15	22.00	27.99	27.99
16	20.00	29.99	29.99
17	18.00	31.96	31.96
18	16.00	33.97	33.97

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[1] Mohr: Lehrbuch der chem. anal. Titrirmethoden, 7 Ed. (1896), 18–19, Fresenius: "Quant. Chem. Analyse," 6 Ed. (1900), Vol. I., 44; For calculations see Watts' Dictionary, Vol. I., p. 248.

Number of reading.	Readings on stationary burette.	Readings on other burette, first series.	Readings on other burette, duplicate series.
19	14.00	35.96	35.96
20	12.00	37.94	37.93
21	10.00	39.93	39.92
22	8.00	41.90	41.90
23	6.00	43.90	43.90
24	4.00	45.90	45.90
25	2.00	47.89	47.89
26	0.00	49.88	49.88
		(v. W.)[1]	(v. W.)[1]

The stationary burette in this experiment was a Mohr burette with a glass stop-cock, and was fitted with an Erdmann float. The other was a simple Mohr burette without a stop-cock or float. The former had a scale 53 cm. long, and the latter, one 61.3 cm. long. The readings were made from one end of the scale to the other, and the duplicate readings were made from the other end back to the starting point. The exact adjustment of the water levels at 0 and 50 at the beginning of the calibration was made with filter-paper, as adjustments of liquids to the marks are made in pycnometers. The next experiment differs from this one only in that a similar burette, but one with a scale as short as is usually to be found in a laboratory, was substituted for the stationary burette in the previous experiment. The length of its scale was 46.3 cm.

The first and the duplicate readings were not made by the same person.

Number of reading.	Readings on stationary burette.	Readings on other burette, first series.	Readings on other burette, duplicate series.
1	0.00	49.95	49.94
2	2.00	47.99	47.98
3	4.00	45.96	45.95
4	6.00	43.95	43.95
5	8.00	41.96	41.95
6	10.00	39.96	39.96
7	12.00	37.99	37.99
8	14.00	35.99	35.99
9	16.00	33.96	33.96

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[1] Experiments are marked (v. W.) or (H.), according as they are carried out by one or the other of us.

Number of reading.	Readings on stationary burette.	Readings on other burette, first series.	Readings on other burette, duplicate series.
10	18.00	31.95	31.95
11	20.00	29.95	29.95
12	22.00	27.96	27.97
13	24.00	25.96	25.97
14	26.00	23.97	23.97
15	28.00	21.97	21.98
16	30.00	19.97	19.97
17	32.00	18.02	18.02
18	34.00	16.02	16.02
19	36.00	14.02	14.02
20	38.00	12.01	12.01
21	40.00	10.00	10.00
22	42.00	8.00	8.00
23	44.00	6.00	6.00
24	46.00	4.00	4.00
25	48.00	1.98	1.98
		(v. W.)	(H.)

In the above experiments the same piece of rubber tubing was used. The next experiment was made with another piece of the same kind of tubing (red) but of a different length. Another simple Mohr burette with a scale-length of 55 cm. and the one with a glass stop-cock used in the first experiment were used. This, along with several other similar experiments, show that the rubber tubing is without influence so far as the duplication of results is concerned.

Number of reading.	Readings on stationary burette.	Readings on other burette, first series.	Readings on other burette, duplicate series.
1	0.00	49.90	49.90
2	2.00	47.90	47.90
3	4.00	45.90	45.90
4	6.00	43.91	43.90
5	8.00	41.94	41.94
6	10.00	39.94	39.94
7	12.00	37.93	37.93
8	14.00	35.92	35.93
9	16.00	33.92	33.93
10	18.00	31.94	31.94
11	20.00	29.96	29.96
12	22.00	27.97	27.98
13	24.00	25.99	25.99
14	26.00	23.99	23.99
15	28.00	22.00	22.00
16	30.00	19.99	19.99

Number of reading.	Readings on stationary burette.	Readings on other burette, first series.	Readings on other burette, duplicate series.
17	32.00	18.00	18.00
18	34.00	16.01	16.01
19	36.00	14.02	14.03
20	38.00	12.05	12.05
21	40.00	10.07	10.08
22	42.00	8.08	8.09
23	44.00	6.10	6.10
24	46.00	4.11	4.11
25	48.00	2.11	2.11
26	50.00	0.11	0.11
		(v. W.)	(v. W.)

The next table shows a comparison of a long Schellbach burette (scale-length 63 cm.) with the Mohr burette used in the previous experiments. These burettes with long scales were used to aid in detecting any possible inaccuracies. Four successive calibrations were made.

Number of reading.	Readings on Schellbach burette.	Readings on other burettes.			
		First series.	Second series.	Third series.	Fourth series.
1	49.50	0.14	0.12	0.12	0.12
2	47.50	2.17	2.15	2.15	2.15
3	45.50	4.19	4.17	4.17	4.18
4	43.50	6.20	6.18	6.18	6.18
5	41.50	8.17	8.15	8.15	8.16
6	39.50	10.19	10.17	10.17	10.18
7	37.50	12.17	12.17	12.17	12.16
8	35.50	14.16	14.14	14.14	14.16
9	33.50	16.12	16.11	16.12	16.11
10	31.50	18.10	18.10	18.10	20.08
11	29.50	20.08	20.08	20.08	22.07
12	27.50	22.07	22.07	22.06	24.07
13	25.50	24.07	24.07	24.06	26.07
14	23.50	26.08	26.07	26.07	28.07
15	21.50	28.08	28.07	28.07	30.07
16	19.50	30.08	30.07	30.07	32.07
17	17.50	32.07	32.06	32.07	34.06
18	15.50	34.06	34.06	34.06	36.07
19	13.50	36.07	36.07	36.07	38.08
20	11.50	38.08	38.07	38.08	40.07
21	9.50	40.06	40.06	40.06	42.05
22	7.50	42.06	42.06	42.06	44.07
23	5.50	44.07	44.07	44.07	46.10
24	3.50	46.09	46.09	46.10	48.10
25	1.50	48.10	48.10	48.10	
26	0.00	49.61		49.61	
		(H.)	(H.)	(H.)	(H.)

Having established that duplicate determinations made under different conditions agree, it seemed advisable to find out whether or not relative calibrations by the above method would lead to the same results as the absolute method. To this end a Mohr burette, with a glass stop-cock, was calibrated by weighing the water it delivered between the marks indicating every 5 cc. The results are given in the following table :

Readings on burette.	Weights of separate quantities of water delivered. Grams.	Total weights of water delivered. Grams.
0.00 to 5.00	4.975	4.975
5.00 to 10.00	4.973	9.948
10.00 to 15.00	4.980	14.928
15.00 to 20.00	4.999	19.927
20.00 to 25.00	4.996	24.923
25.00 to 30.00	4.997	29.920
30.00 to 35.00	4.976	34.896
35.00 to 40.00	4.967	39.863
40.00 to 45.00	5.016	44.879
45.00 to 50.00	5.053	49.932
(H.)	(H.)	

A second Mohr burette with a glass stop-cock was then calibrated against this one, the absolute calibration of which has just been given. In this case a piece of black rubber tubing 117 cm. long, with an external diameter of 7 mm. and an internal diameter of 4 mm., was used. The readings in both burettes were made by the meniscus.

	Readings on stationary burette. (Standard.)	Readings on calibrated burette.	
		First series.	Duplicate series.
1	0.00	49.90	49.90
2	5.00	44.90	44.90
3	10.00	39.90	39.90
4	15.00	34.90	34.90
5	20.00	29.92	29.92
6	25.00	24.96	24.96
7	30.00	19.93	19.93
8	35.00	14.96	14.96
9	40.00	9.94	9.94
10	45.00	4.91	4.91
		(v. W.)	(v. W.)

This second burette was then calibrated by the absolute method. The water was drawn as nearly as possible from between the numbers on its scale gotten by the relative calibrations just given.

Readings on burette.	Weights of separate quantities of water delivered. Grams.	Total weights delivered. Grams.
4.91 to 9.90	4.975	4.975
9.90 to 15.00	5.051	10.026
15.00 to 19.90	4.889	14.915
19.90 to 25.00	5.093	20.008
25.00 to 29.90	4.935	24.943
29.90 to 34.90	5.019	29.962
34.90 to 39.90	4.964	34.926
39.90 to 44.90	4.976	39.902
44.90 to 49.90	4.995	44.897
(H.)	(H.)	

Reference to the table of the relative calibrations of this burette will show that the water delivered by it between the marks 4.91 and 49.90 should weigh the same as the water delivered by the other burette between the marks 0.00 to 45.00 on its scale. The experiment has been given which shows that the first burette delivers 44.879 grams from 0.00 to 45.00, and the experiment just given shows that the second burette delivers 44.897 grams from 4.91 to 49.90. The difference is 0.018 gram.

The next table makes possible a comparison of the delivering capacity of the second burette as predicted upon the basis of the five relative calibrations against the first burette as a standard. This first burette, it will be recalled, was calibrated by the absolute method.

The accuracy which this table indicates could doubtless be increased by making the readings with a cathetometer. We consider it sufficiently accurate without this aid, for the error in reading burettes, such as are in general use, cannot fairly be considered as less than ±0.01 cc.

We anticipated this accuracy in the method. In principle, the errors involved in its application should not exceed those necessary in reading burettes. It permits each point in the calibration to be fixed as accurately as the most sensitive re-

Readings on standard burette.	Corresponding readings on uncalibrated burette, gotten by relative calibrations.	Corresp'd'g weight of water delivered by standard burette. Grams.	Corresp'd'g weight of water delivered by uncalibrated burette. Grams.	Difference between weight predicted and weight found. Grams.	Total weights of water delivered by standard burette. Grams.	Corresponding total weights of water delivered by uncalibrated burette. Grams.	Difference between total weights delivered. Grams.
0.00– 5.00	49.90–44.90	4.975	4.995	0.020	4.975	4.995	0.020
5.00–10.00	44.90–39.90	4.973	4.976	0.003	9.948	9.971	0.023
10.00–15.00	39.90–34.90	4.980	4.964	0.016	14.928	14.935	0.007
15.00–20.00	34.90–29.92	4.999	4.999	0.000	19.927	19.934	0.007
20.00–25.00	29.92–24.96	4.996	4.995	0.001	24.923	24.929	0.006
25.00–30.00	24.96–19.93	4.997	5.023	0.026	29.920	29.952	0.032
30.00–35.00	19.93–14.96	4.976	4.959	0.017	34.896	34.911	0.015
35.00–40.00	14.96– 9.94	4.967	4.971	0.004	39.863	39.882	0.019
40.00–45.00	9.94– 4.91	5.016	5.015	0.001	44.879	44.897	0.018
	(v. W.)	(H.)	(H.)				

versible end-reaction for which the burettes may be subsequently used, for by simply changing the relative levels back and forth one may fix each reading beyond readable error. The practice of duplicating by running the water, and the readings, backward through the same series of measurements balances errors that may arise from the necessarily unequal rates at which the water is delivered from one burette to the other between the different readings, thus insuring that no more than the normal amount of water has been left behind on the burette walls at any point, and furnishing duplicate readings whose agreement does not depend upon an accidental equality in the rate at which the two calibrations are made. It is, lastly, free from errors that may enter a method that depends upon the use of rubber tubing under different pressures. For example, when a piece of rubber tubing, such as we have used, 5 cm. long and closed at one end, is joined to the tip of a burette with a glass stop-cock, and both the burette and tubing are entirely filled with water, there is a readable difference in the level of the water, depending upon whether its weight is supported by the glass (when the stop-cock is closed) or by the rubber (when the stop-cock is opened). Such errors are variable and may be reduced, doubtless, by using thick rubber tubing and by having as few joints as possible made with it, but the method we have described avoids such errors entirely.

The precautions we have observed in the use of the method are not many. We have avoided the use of a float in the burette that is moved up and down in the course of a calibration, for it is well known that a float may readjust itself under the influence of changes in the position of a burette so that its axis is at quite a different angle to the axis of the burette from what it was originally. We have used a piece of tubing that was not too short. If the tubing is so short, or the burettes mounted so far apart that, in any of the positions they assume in the course of a calibration, the rubber is drawn or stretched, it is to be expected that errors may enter. Our general practice has been to so select the length of tubing and so arrange the burettes that beneath each a length of about 20 cm. always hangs vertically. We have always arranged the apparatus near the edge of a table-top so that the tubing hangs free beneath the burettes, and throughout the calibration does not come in contact with anything that might help support its weight or alter its volume. Lastly, we have made the duplicate calibration soon after the first one, for it is to be expected that if a sufficient time be allowed to intervene between the two sets of measurements the walls of the burette that is almost empty would dry and in the duplicate calibration the burette would seem to hold as much too much water as would be required to wet its walls again.

By this method it is possible to calibrate at as many or few points as may be desirable. The average time required to calibrate a burette at every 2 cc. and to duplicate it with the accuracy described in this paper, is about one and a half hours.

The same principle can, of course, be used in calibrating pipettes, and for the graduation of apparatus made for special volumetric purposes.

CHEMICAL LABORATORY,
BRYN MAWR COLLEGE,
March 4, 1903.

Contributions from the Chemical Laboratory of the Nebraska Wesleyan University.

V.—THE ACTION OF ALKALINE SULPHIDES UPON *p*-NITROBENZYLANILINE.

BY FREDERICK J. ALWAY AND ARTHUR B. WALKER.

p-Nitrobenzylaniline has been shown to undergo simultaneous reduction and oxidation when treated with alkaline sulphides in alcoholic solution,[1] *p*-amidobenzylideneaniline being formed. The reduction has been considered to take place according to the following equation:

$$2NO_2.C_6H_4.CH_2.NH.C_6H_5 + Na_2S = Na_2SO_4 + 2NH_2.C_6H_4.CH : N.C_6H_5.$$

While preparing *p*-amidobenzylideneaniline by the above method we noticed that in one case crystals of *p*-azoxybenzylideneaniline were formed, while in many previous preparations there had been no formation of crystals, *p*-amidobenzylideneaniline being soluble in alcohol. The investigation on which we now report was undertaken in order to determine the conditions under which alkaline sulphides convert *p*-nitrobenzylaniline into *p*-azoxybenzylideneaniline.

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[1] Chem. Centrbl., 1899, I., 238; D. R. P., No. 99,542.

We have found that when the sulphide is allowed to act upon the nitrobenzylaniline in the proportion of 1 molecule of the former to 8 molecules of the latter, the alcoholic solution being kept very gently boiling, the maximum yield of *p*-azoxybenzylideneaniline is obtained, *viz.*, about 75 per cent of the theoretical amount. With an increasing proportion of sulphide the yield steadily diminishes until only *p*-amidobenzylideneaniline is obtained. The insoluble *p*-azoxybenzylideneaniline, when boiled for some time with an alcoholic solution of sodium sulphide, is converted into a compound similar in properties and reactions to *p*-amidobenzylideneaniline. The formation of *p*-azoxybenzylideneaniline by the action of caustic alkalies upon the alcoholic solution of *p*-nitrobenzylaniline was likewise investigated quantitatively in order to determine the proportions required to produce the maximum yield. This is obtained when the substances are used in the proportion of 1 molecule of alkaline hydroxide to 4 molecules of *p*-nitrobenzylaniline. An increased proportion of alkali does not increase the yield, but, on prolonged boiling, decomposes the *p*-azoxybenzylideneaniline already formed. When it is desired to obtain the last-mentioned compound, the use of the caustic alkali is much to be preferred on account of the rapidity and certainty of its action.

Incidentally, we have endeavored to determine the best method of preparing *p*-nitrobenzylaniline, avoiding as far as possible the formation of *bis*-*p*-nitrobenzylaniline. Strakosch[1] prepared the former compound by heating a mixture of *p*-nitrobenzyl chloride and an excess of aniline to boiling for a few minutes. He isolated only the one compound. Paal and Sprenger[2] have since obtained the same compound, together with *bis*-*p*-nitrobenzylaniline, by heating *p*-nitrobenzyl chloride (1 molecule) with aniline (2 molecules) in concentrated alcoholic solution for six hours. The solid obtained by pouring the crude reaction-mixture into cold water was separated by treatment with hot dilute alcohol into its component compounds, the *bis-p*-nitrobenzylaniline remaining undissolved. They obtained 70 per cent of the theoretical yield of *p*-nitrobenzylaniline and a small yield of the other compound, the amount not being given. Not long since one of us[1] showed that *p*-azoxybenzylideneaniline and the three analogous toluidines may be obtained in equally good yield directly from *p*-nitrobenzyl chloride, aniline or a toluidine, and a caustic alkali, if the mixture is heated to boiling one minute. We have now found that a prolonged heating of the two compounds is not necessary in order to obtain the maximum yield of *p*-nitrobenzylaniline. If the mixture of the two, in the proportions used by Paal and Sprenger,[2] be heated on the water-bath for two or three minutes, the yield of *p*-nitrobenzylaniline is 92 per cent of the theoretical amount, and that of *bis-p*-nitrobenzylaniline only from 1 to 2 per cent. When the mixture of *p*-nitrobenzyl chloride and aniline, without addition of alcohol, is heated to boiling it is necessary to have a great excess of aniline. In all cases, however, small amounts of *bis-p*-nitrobenzylaniline are formed. Under various circumstances this dissolves in ordinary alcohol and, therefore, is liable to escape detection.

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[1] Ber. d. chem. Ges., **6**, 1062.

[2] *Ibid.*, **30**, 69.

No sulphate was detected in the reaction-mixtures obtained by boiling *p*-nitrobenzylaniline or *p*-azoxybenzylideneaniline with an alcoholic solution of sodium sulphide. The explanation of the reduction, referred to above, is evidently incorrect.

EXPERIMENTAL.

Preparation of p-Nitrobenzylaniline.

The method of Paal and Sprenger was first tried. A mixture of *p*-nitrobenzyl chloride (1 mol.) and aniline (2 mols.) was dissolved in the minimum quantity of alcohol (95 per cent) and heated on the water-bath for six hours. After repeated preparations by this method it was found that, while the solution usually remained clear until the end, at times after the heating had continued about five hours, large crystals of *bis-p*-nitrobenzylaniline began to separate out, and at the end of another hour the solution contained very little of this compound. When the reaction-mixture was poured into ice-water and the solid, so obtained, was treated with boiling ordinary alcohol, the whole of it dissolved. By continuing the boiling with alternate additions of water and alcohol, the *bis-p*-nitrobenzylaniline was caused to separate out as a yellow powder. It proved more satisfactory to treat the crude product with 70 per cent alcohol. This dissolved the *p*-nitrobenzylaniline and only a very small quantity of the other compound. One gram of *bis-p*-nitrobenzylaniline dissolved in 1200 cc. boiling 70 per cent alcohol. On cooling 0.35 gram separated from the solution.

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[1] Ber. d. chem. Ges., 35, 2435.

[2] *Loc. cit.*

When a mixture of *p*-nitrobenzyl chloride (1 mol.) and aniline (2 mols.) was heated on the water-bath it first melted to a clear liquid of a brownish-red color. Within two minutes this liquid became semi-solid on account of the formation of aniline hydrochloride. This compound, after being filtered out and washed with ether, was identified by its melting-point and its reactions. The hydrochloride of *p*-nitrobenzylaniline could not be detected in the reaction-mixture. When, instead of warming the mixture on the water-bath, it was heated in a flask over a flame, the reaction was the same when the temperature was not raised above 120°. But, as soon as it was raised above this point, without further application of heat, the temperature rose rapidly to 185°, the mass becoming an intense red in color. As we were unable to isolate *p*-nitrobenzylaniline from this red mass we have not investigated it further. When the temperature was not allowed to rise above 140° none of the red substance was formed. When a great excess of aniline (4 to 6 mols.) was used and the whole heated to boiling (one to two minutes) the same good yield, about 92 per cent, of *p*-nitrobenzylaniline was obtained. The excess of aniline was removed either by treatment with dilute aqueous hydrochloric acid or by distillation with steam, the *p*-nitrobenzylaniline being insoluble in the dilute acid and non-volatile with steam. In an experiment that was performed to determine the yield of *p*-nitrobenzylaniline, *p*-nitrobenzyl chloride (10 grams) was mixed with aniline (11.2 grams) and heated on the water-bath five minutes. The semi-solid reaction-product was treated with boiling 70 per cent alcohol. The yield of *bis-p*-nitrobenzylaniline was 0.15 gram. The crystals of *p*-nitrobenzylaniline weighed 9.5 grams. To determine the amount of the last compound remaining dissolved in the alcoholic filtrate, the latter was heated and then treated with alcoholic potash. The *p*-azoxybenzylideneaniline so obtained weighed 2 grams. Ten grams of pure *p*-nitrobenzylideneaniline, under similar treatment, yielded 7.5 grams *p*-azoxybenzylideneaniline. The filtrate must have contained 2.7 grams of the former compound in solution. Accordingly, 10 grams of *p*-nitrobenzyl chloride yield 12.2 grams of *p*-nitrobenzylaniline, or 92 per cent of the theoretical amount.

Action of Caustic Alkalies upon p-Nitrobenzylaniline.

When the hot solution of this compound in ordinary or in absolute alcohol is treated with sodium hydroxide or potassium hydroxide in the solid form, or in either aqueous or alcoholic solution, or with sodium or potassium ethylate, the solution very rapidly darkens in color. When it has become almost black a very rapid separation of lustrous golden-yellow crystals takes place. At the end of a few minutes the reaction is complete. Small quantities of *p*-nitrobenzylaniline may be detected by this reaction. The crude reaction-products containing *p*-nitrobenzylaniline may be used in the same manner, without previous purification. In the latter case, however, it is necessary to use dilute alcohol as a solvent and to add an extra amount of alkali in order to neutralize the hydrochloric acid which occurs in the mixture as aniline hydrochloride. Hot alcoholic solutions of *p*-nitrobenzylaniline were treated with potassium hydroxide solution and the resulting *p*-azoxybenzylideneaniline was filtered out, washed well with alcohol, dried, and weighed. The yield reached a maximum when the compounds were used in the proportion indicated above, *viz.*, 1 molecule of the hydroxide to 4 of the other compound. When smaller proportions of alkali were used, unchanged *p*-nitrobenzylaniline could be obtained from the filtrate. By prolonged heating of the *p*-azoxybenzylideneaniline with an excess of alkali it was entirely decomposed, forming a red solution, which, on treatment with water, gave a red precipitate.

Action of Alkaline Sulphides upon p-Nitrobenzylaniline.

The gently boiling alcoholic solution of *p*-nitrobenzylaniline was treated with an alcoholic solution of sodium sulphide, only small amounts being added at a time. Within from three to ten minutes the characteristic separation of crystals of *p*-azoxybenzylideneaniline began. They separated out much more slowly than when the alkaline hydroxides were used. The maximum yield was obtained when the two compounds were used in the proportion of 8 molecules of the former to 1 of the latter. When a higher proportion of sodium sulphide was used the yield was less and usually no separation of crystals took place. *p*-Azoxybenzylideneaniline was dissolved by prolonged boiling with sodium sulphide and alcohol. The solution gave a precipitate with water. In properties and reactions this was similar to *p*-amidobenzylideneaniline. To have fully identified this compound an analysis would have been necessary. This was not made. The alcoholic filtrates obtained by the action of sodium sulphide upon the above-mentioned compounds were evaporated to dryness and the residues treated with hot water. The clear aqueous filtrates gave no precipitate with barium chloride.

UNIVERSITY PLACE, NEBRASKA,
March 14, 1903.

Contributions from the Chemical Laboratory of the Nebraska Wesleyan University.

VI.—THE RELATIONS EXISTING BETWEEN THE PHYSICAL PROPERTIES AND THE MOLECULAR WEIGHTS OF *p*- AND *m*-NITROSOBENZALDEHYDE.

BY FREDERICK J. ALWAY AND WALTER D. BONNER.

A year since, in an article by Alway and Welsh,[1] it was pointed out that while *m*-nitrosobenzaldehyde forms white crystals and is readily volatile with steam, the isomeric *p*-nitrosobenzaldehyde forms yellow crystals and at times cannot be distilled with steam, but passes over rapidly when, by the addition of calcium chloride, the temperature of the mixture in the flask through which steam is being passed is raised to the melting-point of *p*-nitrosobenzaldehyde, *viz.*, 137°. Likewise, this compound was found to volatilize readily when its green solutions, *e. g.*, in acetic acid and in alcohol, were subjected to the action of steam. It was mentioned, also, that both aldehydes are green in the liquid state and in solution, and that when volatilized with steam they give the characteristic odor of nitroso compounds.

Since that time Piloty[2] has practically completed the proof of the dependence of the green or blue color upon the monomolecular condition and of the white or colorless form upon the dimolecular condition. A large number of aliphatic nitroso compounds have been prepared by Piloty, and many more aromatic nitroso compounds by Bamberger and others. So far as we are aware, *p*-nitrosobenzaldehyde is the only compound in which a nitroso group is attached to a carbon atom, that is known to exist in the form of yellow crystals. For this reason it seemed desirable to determine its molecular weight both in cold and in hot solutions.

Piloty,[3] in describing some new nitroso compounds in 1898, stated that "these nitroso compounds, like all known substances of this class, show the ability to form colorless solids, which, in solution and in the liquid state, are an intense blue (or green) in color, a property which can be used for the recognition of true nitroso compounds, and which was first observed by Victor Meyer in the case of the pseudonitrols.'' (This statement was not correct, as the exception, *p*-nitrosobenzaldehyde[1] had already been described.) Soon after, the same investigator obtained brom-2-nitroso-2-propane[2] as a blue liquid at ordinary temperatures and, further, showed that, when in the colorless form, the nitroso compounds are able to form colorless solutions, the freezing-points of which indicate a dimolecular condition, but that, on warming, the color changes to blue or green, the molecular weight determinations of the latter showing that the monomolecular condition prevailed. About the same time Brühl,[3] finding that a 53 per cent supersaturated alcoholic solution of nitrosobenzene did not possess as intense a green color as 22 and 12 per cent solutions of the same compound in benzene, suggested that in the latter the nitrosobenzene was in a monomolecular condition and in the former in the dimolecular condition, as expressed by the formula :

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[1] J. Am. Chem. Soc., **24**, 1052 (1902).

[2] Ber. d. chem. Ges., **35**, 3090; Piloty and Stock: *Ibid.*, **35**, 3093; Piloty and Steinbock: *Ibid.*, **35**, 3101. See also Schmidt: *Ibid.*, **35**, 2323, 3727, 3737.

[3] *Ibid.*, **31**, 218 (1898).

$$\begin{array}{l} C_6H_5.N.O \\ \qquad\quad \dot{O}.\dot{N}.C_6H_5 \end{array}$$

He found the molecular refraction to agree with this assumption and suggested that there was a direct connection between the green color of nitroso compounds in general and the monomolecular condition. Bamberger and Rising[4] have determined the molecular weights of a large number of nitroso compounds and have found that those that form deep-green solutions in the cold contain simple molecules both in boiling and in freezing solutions. On the other hand, nitrosomesitylene and 2.6-dimethylnitrosobenzene, which form faintly green solutions in the cold, the latter becoming an intense green on warming, exist chiefly in the dimolecular condition in cold solutions but in the monomolecular condition in hot solutions.

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[1] Ber. d. chem. Ges., **29**, 3037 (1896).

[2] *Ibid.*, **31**, 452, 457 (1898).

[3] *Ibid.*, **31**, 1465 (1898).

[4] *Ibid.*, **33**, 3877 (1901).

A few nitroso compounds form blue or green crystals, *viz.*, 3.4-dimethylnitrosobenzene,[1] brom-2-nitroso-2-dimethyl-3.3-butane,[2] *o*-nitrosoanisol, *p*-nitrosoanisol,[3] 1.4-dibrom-1.4-dinitrosocyclohexane, and 1.4-dichlor-1.4-dinitrosocyclohexane.[4] The last-mentioned compound, under the influence of hydrochloric acid, changes to the isomeric 1.4-dichlor-1.4-*bis*-nitrosylcyclohexane. The latter is colorless and does not form a green liquid or green solutions. It is considered by Piloty[5] to form the transition between those dimolecular nitroso compounds that decompose into monomolecular nitroso compounds only in boiling solutions, and the *bis*-nitrosyl compounds, like *bis*-nitrosylbenzyl[6] and *bis*-nitrosylcarvon,[7] which are odorless and non-volatile, and are blue or green neither in solution nor in the liquid state.

We have found that in boiling benzene both the *p*- and the *m*-nitrosobenzaldehyde show the normal molecular weight. The same is true in freezing acetic acid. In freezing benzene the former shows the monomolecular condition, but the latter gives evidence of a part being in the dimolecular condition. The decrease in the intensity of the green color of the solution of *m*-nitrosobenzaldehyde in benzene as the freezing-point of the latter is approached is in accord with the change in molecular weight. A change in the intensity of the color of solutions of *p*-nitrosobenzaldehyde, on the other hand, is accompanied by the separation of yellow crystals. The molecular weight determinations show that *m*-nitrosobenzaldehyde, rather than *p*-nitrosobenzaldehyde,[8] resembles nitrosomesitylene. No light is thrown by these determinations, however, upon the cause of the peculiar position that *p*-nitrosobenzaldehyde occupies among the nitroso compounds.

In experiments 5, 6, and 7 the compound dissolved very slowly in cold benzene. After the addition of the first weight

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[1] Ann. Chem. (Liebig), **316**, 285 (1901).

[2] Piloty: Ber. d. chem. Ges., **35**, 3092 (1902).

[3] v. Baeyer and Knorr: *Ibid.*, 3034 (1902).

[4] Piloty and Steinbock: *Ibid.*, **35**, 3101 (1902).

[5] *Ibid.*, **35**, 3101 (1902).

[6] Ann. Chem. (Liebig), **263**, 212.

[7] v. Baeyer: Ber. d. chem. Ges., **28**, 642 (1895).

[8] J. Am. Chem. Soc., **24**, 1054 (1902).

Experiment number.	Solvent.	Dissolved substance.	Weight of solvent in grams.	Weight of dissolved substance in grams.	Percentage strength of solution.	Depression of freezing-point.	Elevation of boiling-point.	Molecular weight.
1	Benzene	*p*-Nitrosobenzaldehyde	107.2478	0.5938	0.554		0°.120	124.7
2	"	"	"	1.9596	1.83		0°.360	137.4
3	"	"	"	2.6912	2.51		0°.495	136.9
4	"	"	"	3.2404	3.02		0°.605	134.9
5	"	"	17.2762	0.1004	0.581	0°.250		116.2
6	"	"	"	0.1506	0.871	0°.345		123.7
7	"	"	"	0.2588	1.50	0°.590		127.1
8	Acetic acid	"	20.5882	0.1280	0.622	0°.215		112.4
9	"	"	"	0.2110	1.025	0°.335		119.3
10a	"	"	"	0.3140	1.53	0°.365		163.4
10b	"	"	"	"	"	0°.525		113.7
11	Benzene	*m*-Nitrosobenzaldehyde	116.1494	0.7142	0.615		0°.130	127.7
12	"	"	"	0.9932	0.855		0°.170	135.8
13	"	"	"	1.3196	1.136		0°.215	142.7
14	"	"	"	1.5855	1.365		0°.260	141.8
15	"	"	17.2762	0.0602	0.348	0°.105		165.9
16	"	"	"	0.0968	0.560	0°.165		169.7
17	"	"	"	0.1438	0.832	0°.310		134.2
18	"	"	"	0.2658	1.538	0°.570		134.9
19	Acetic acid	"	20.5882	0.0672	0.336	0°.110		115.6
20	"	"	"	0.1484	0.721	0°.225		124.9

Theoretical molecular weight of nitrosobenzaldehyde = 135.

and continued stirring for one hour very little had dissolved. A determination of the freezing-point showed a depression of 0°.05. Then the solvent was warmed to about 60° to dissolve the substance. This had to be repeated after the addition of each new portion. No crystals separated from the solution on cooling.

In experiment 10a crystals separated out before the solution began to solidify. The whole was warmed until the crystals redissolved and then cooled down again (Experiment 10b). No separation of crystals of the dissolved substance took place in this case.

In Experiments 15, 16, 17, and 18 the solvent was warmed to dissolve the nitrosobenzaldehyde. In 15 and 16 the color of the solution, which was a deep green when warm, became much fainter as the temperature approached the freezing-point of the solvent, but returned to its former intensity on warming. In Experiments 17 and 18 no such change in the color was observed.

Naphthalene is not available as a solvent in the molecular weight determinations of the nitrosobenzaldehydes, as the green color of the solutions rapidly changes to a red, showing that a chemical change has taken place. A similar change takes place when the aldehydes are boiled with benzene for a long time.

Saturated solutions of the two nitrosobenzaldehydes in ether, benzene, and acetic acid were prepared. Part of each was heated to boiling and another part cooled to 0°. The only case in which a distinct change in the color was noticeable was that in which the benzene solution of *m*-nitrosobenzaldehyde was cooled, the green color becoming much fainter.

UNIVERSITY PLACE, NEBRASKA,
April 25, 1903.

THE ACTION OF PHOSPHONIUM IODIDE ON POLYCHLORIDES.[1]

[FIRST PAPER.]

BY ERNESTINE AND PETER FIREMAN.

Since Liebig,[2] in 1832, took up the study of the action of gaseous ammonia or ammonium chloride on phosphorus pentachloride, a study which led him to the discovery of "chlorophosphuret of nitrogen," a number of chemists[3] have, from time to time, attacked this subject. However, until very recently, little light was thrown on the reaction in question. The yield was very bad, and the relation of the chlorophosphuret to other phosphorus compounds remained unestablished. Our knowledge of the products of the action of sal ammoniac or gaseous ammonia on the pentachloride of phosphorus was in this unsatisfactory state when H. N. Stokes, in 1895, began the investigation of this subject. One of the first results of his investigation[4] was the isolation, from the products of the reaction, of a new chloronitride with the composition $(PNCl_2)_4$ and of an oily chloronitride with the same percentage composition, whose molecular weight remained undetermined. These two bodies were obtained in addition to Liebig's chlorophosphuret $(PNCl_2)_3$. In his earlier experiments Stokes prepared the chloronitrides of phosphorus by the method, described by Gladstone,[5] of distilling phosphorus pentachloride with a large excess of ammonium chloride. But in 1897 he devised a new method[6] which gives an almost theoretical yield. It consists in heating a mixture of ammonium chloride and phosphorus pentachloride in the proportion of their molecular weights in a sealed tube. From the reaction-products Stokes was able to isolate, by distillation under diminished pressure, the following series of polymeric chloronitrides:

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[1] The present communication contains a part of the results of an investigation carried out in 1900, at the Columbian University, Washington, D. C.

[2] Ann. Chem. (Liebig), **11**, 146.

[3] In his first article "on the chloronitrides of phosphorus" (This JOURNAL, **17**, 275) H. N. Stokes quotes the literature on this subject.

[4] *Loc. cit.*

[5] Q. J. Chem. Soc., **3**, 135; Ann. Chem. (Liebig), **76**, 76.

[6] This JOURNAL, **19**, 782.

$$(PNCl_2)_3,\ (PNCl_2)_4,\ (PNCl_2)_5,\ (PNCl_2)_6,\ (PNCl_2)_7, \text{ and } (PNCl_2)_x.$$

In view of the smoothness of the reaction between phosphorus pentachloride and ammonium chloride and the remarkable nature of the resulting chloronitrides and of the products of their saponification, it has appeared desirable to determine by investigation whether we have here a unique reaction, without analogues, or a typical representative of a whole class. It has appeared desirable, in other words, to ascertain whether ammonium chloride would not act upon other inorganic polychlorides in a similar manner. On the other hand, it has seemed of interest to compare the action of a phosphonium halide upon polychlorides with that of ammonium chloride upon them. The former problem has been taken up by one of us and E. G. Portner, while the latter the present writers have attempted to study. The following is a description of some of the results obtained by them.

Since phosphonium chloride and phosphonium bromide are practically inaccessible in quantities necessary for an extended research, only phosphonium iodide is available for an investigation of this kind.

It must be confessed that at the inception of this research the hope was entertained that the action of phosphonium iodide upon the polychlorides would resemble to a greater or less extent that of ammonium chloride upon them. It was hoped that by treating bodies such as antimony pentachloride or tin tetrachloride with phosphonium iodide, compounds would result resembling the chloronitrides of phosphorus, but containing, in place of phosphorus, antimony or tin, and in place of nitrogen, phosphorus. This expectation appeared to be justified by the fact that a compound consisting of tin, phosphorus, and chlorine was described by R. Mahn,[1] who prepared it by the action of hydrogen phosphide upon stannic chloride. To be sure, the composition assigned to that body

[1] Jenaische Ztschr. f. Medicin u. Naturwiss., 5, 158.

was rather strange, *viz.*, $Sn_3P_2Cl_6$; but an incorrect formula was also ascribed to Liebig's chlorophosphuret for a long time. It therefore became an additional incentive to the carrying out of this investigation to verify, if possible, Mahn's results, and perhaps to correct the formula for the body he obtained.

Actual experiments soon demonstrated, however, that the action of phosphonium iodide on the polychlorides is radically different from that of ammonium chloride on these chlorides; that the analogues of the chloronitrides, with phosphorus in place of nitrogen, cannot, if at all, be prepared through the aid of phosphonium iodide. However, the action of phosphonium iodide on the tetra- and pentachlorides, such as it is, has appeared well worthy of careful study.

In accordance with the original object of this investigation, the lowest polychlorides[1] which could fall within its scope are the tetrachlorides. The common tetra- and pentachlorides were, therefore, first attacked, but the nature of the results obtained seems to justify the extension of this study so as to include also some lower polychlorides.

I.

Action of Phosphonium Iodide on Antimony Pentachloride.

The experiments described below show that when phosphonium iodide and antimonic chloride are heated in a sealed tube a reaction takes place between them which can be represented by the following equation:

$$3SbCl_5 + 3PH_4I = SbI_3 + 2SbCl_3 + 9HCl + PH_3 + P_2.$$

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[1] It is evident that for a reaction similar to that which takes place between phosphorus pentachloride and ammonium chloride, no lower chlorides than tetrachlorides can be used in place of phosphorus pentachloride. For, as Stokes shows, the chloronitrides of phosphorus result according to this equation:

$$PCl_5 + NH_4Cl = 4HCl + PNCl_2.$$

Now, with ammonia, which can be used in place of ammonium chloride, the reaction must be as follows:

$$PCl_5 + NH_3 = 3HCl + PNCl_2.$$

Hence it is obvious that only chlorides of such elements which carry at least 4 atoms of chlorine to 1 of their own, can give off 3 atoms of chlorine to form 3 molecules of hydrochloric acid with the hydrogen of ammonia, and still retain chlorine:

$$CCl_4 + NH_3 = 3HCl + CNCl.$$

In this reaction antimonic chloride is reduced to antimonous chloride, a third of the latter being converted into antimonous iodide, copious quantities of hydrochloric acid gas and some hydrogen phosphide are evolved, and phosphorus is set free.

Antimony pentachloride and phosphonium iodide, when brought together in the open air at ordinary temperature, act upon one another with explosive violence, and free iodine escapes with the other gases.

In order to seal up together antimonic chloride and phosphonium iodide, it is necessary to place one of these substances in a narrow tube, and then place this narrow tube within a larger tube, into which the other substance has been previously introduced.

In studying the reaction under consideration we proceeded as follows: The phosphonium iodide was placed in an ordinary bomb tube, into which the antimonic chloride, contained in a short, narrow tube, was then introduced. Digestion at the temperature of boiling water is sufficient to bring about the reaction indicated above. It is advisable, however, to heat at a somewhat higher temperature in order to hasten matters. It may perhaps be well to describe one experiment in detail.

Four tubes, each containing 3 cc. (6.8 grams) of antimony pentachloride (1 mol.) and 3.6 grams of phosphonium iodide (1 mol.), were heated for five hours at 95° to 105°. On cooling, the contents of the tube consisted of some unchanged phosphonium iodide (which remained at the bottom), of a solid mass partly orange-yellow and partly ruby-red in color, and of some liquid (apparently unchanged antimonic chloride). On opening the tubes, hydrogen chloride escaped. The loss of weight in the four tubes was 1.7, 1.6, 1.9, and 1.8 grams respectively.

On further digestion for five hours at 100° to 110°, the entire contents of the tubes became solid. No phosphonium iodide was now to be discerned, and the color of the mass was yellow and orange. On opening, the tubes were found to have lost 0.6, 0.65, 0.2, and 0.4 gram, respectively.

Heating for nine hours more at 100° to 110° caused in two of the tubes only an additional loss of 0.1 gram of gas. The total loss in the four tubes was 2.4, 2.25, 2.2, and 2.2 grams, respectively.

In other experiments the tubes were opened more frequently, and the gradual disappearance of the phosphonium iodide and antimony pentachloride could be well observed. The former remained at the bottom of the tube in an entirely detached mass from the rest of the substance, while the latter remained liquid, but was rendered dark in color. Some of the gas escaping, on opening the tubes, was collected each time in a flask, with some water, and examined. At the earlier stages nothing but hydrochloric acid escaped. The precipitate with silver nitrate was perfectly white and dissolved easily and completely in ammonia. Towards the end of the operation, at the last opening or two, the outrushing gas flashed up, thus showing the formation of phosphine.

Larger quantities of the material than were used in the tubes of the experiments described above can be heated in one tube with entire safety, but then the tubes must be opened more frequently and after shorter intervals. The digestion should be so regulated that not more than 2 grams of hydrochloric acid gas will be present at one time in a tube of medium capacity.

There being no other more convenient way to get out the product of the reaction from the tubes, the latter were cut into pieces, from which as much as possible of the substance was then scraped out and collected separately in a flask (these were styled Portion I.). The pieces of the tube, with what adhered to them (Portion II.), were placed in another flask. Portion II. was first treated with solvents. It, together with the pieces of glass, was covered with benzene and heated for some time in a water-bath with a reflux condenser. The liquid was then filtered hot into the flask containing Portion I. The residue of Portion II. was again digested with benzene with the reflux condenser, and the liquid filtered into the flask containing Portion I. This treatment was repeated once more. The benzene solution, together with the main portion of the product, was now heated on the water-bath with a return condenser, and the liquid filtered hot into a flask. The residue was treated twice more with benzene. The united filtrates were then concentrated to about 300 cc. by distillation and then allowed to cool in a stoppered flask. Crystals separated which were mostly red in color, flat, and united into bands. Some small, yellow, square crystals were also formed. The liquid was poured off and the crystals, which weighed 5.5 grams, were redissolved in benzene and recrystallized. A red substance was obtained which, on drying in the desiccator, and for a short time in the steam-oven, proved to be pure antimony triiodide. It was identified by its melting-point (167°) and by analysis, as follows:

I. 0.3264 gram substance gave 0.1112 gram Sb_2S_3, corresponding to 0.0798 gram antimony.

II. 0.2442 gram substance gave 0.3412 gram AgI, corresponding to 0.1844 gram iodine.

	Calculated for SbI_3.	Found.
Sb	24.28	24.45
I	75.72	75.49

The filtrate, after the removal of the first crop of crystals (5.5 grams) was considerably concentrated by distillation and allowed to stand in a stoppered flask. After some time crystals separated, which were in the main yellow, but in a few instances red. The two kinds of crystals (aggregating 3 grams) proved to be two modifications of antimony triiodide. They showed the same melting-point (167°), and the yellow modification passed over into the red one when it was attempted to recrystallize it.

On further concentrating the mother-liquor, two more grams of antimonous iodide (identified by its melting-point) were obtained. The remaining solution was reduced to a small bulk and allowed to get cold. A white, crystalline cake formed. Instead of pressing out from the cake the remaining benzene and so separating the white crystalline mass from the mother-liquor by filtering with suction, all the benzene was distilled off and the solid mass transferred to a distilling-flask. The latter operation was easily carried out by melting the residue by gently warming and then pouring. The white solid distilled over for the most part at about 224°. By its easy fusibility and its boiling-point it was shown to be antimonous chloride.[1] The last portion of the distillate was somewhat contaminated with some antimonous iodide which had remained to the last in the benzene solution, and which, though distilling at a much higher temperature (414° to 427°), sublimes at a considerably lower temperature. About 11 grams of antimonous chloride were obtained.

The residue which remained from the main portion of the product, after it was treated with benzene, as well as the one which remained from that portion of the product which adhered to the glass, was treated with carbon disulphide in a water-bath with a reflux condenser in order to remove the residue of antimonous iodide. The filtered solution gave, on concentration, about two more grams of the latter.

The final residue (the free one and the one adhering to the glass), was a bright-red powder which responded to the various tests for red phosphorus. It took fire when touched with a hot glass rod, and when heated in a small tube, closed at one end, it formed yellow phosphorus. It dissolved in nitric acid, and the solution, when treated with magnesia mixture in the usual way, gave the characteristic precipitate for phosphoric acid. A quantitative determination of the phosphorus was attempted, but, as is well known, the complete oxidation of red phosphorus is a very slow process. After repeated treatment with dilute and concentrated nitric acid, alternately, and evaporating to dryness, not more than about 70 per cent of phosphorus was found. It did not seem necessary to pursue the estimation of phosphorus any further, since even the imperfect analysis made proved that we had in hand phosphorus, although it was associated with the accumulated impurities of the various operations. About 1.5 grams of the red phosphorus were obtained from the main portion of the reaction-product. The phosphorus which adhered to the glass probably amounted to about 0.5 gram.

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[1] The boiling-point of antimonous chloride is variously stated. It is given by some as 216° and by others as 223°.5. A perhaps not uninteresting observation was made in this laboratory which may explain this discrepancy. A freshly obtained quantity of antimony trichloride, which distilled over with great constancy at about 224°, showed, after a few weeks, with just as much constancy the boiling-point 216°.

In concluding the description of the experimental part of the study of the action of phosphonium iodide upon antimony pentachloride, it may be added that the antimony was determined as Sb_2S_3 in the usual way, while the iodine was precipitated from a tartaric acid solution to which a weighed amount of silver nitrate in very slight excess was added.[1]

The experiments described above seem to be very satisfactorily represented by the equation :

$$3SbCl_5 + 3PH_4I = SbI_3 + 2SbCl_3 + 9HCl + PH_3 + P_2.$$

1. The antimonic chloride and phosphonium iodide were used in the proportion of 1 molecule to 1 molecule as required by the equation.

2. The antimony was actually obtained in the form of antimonous iodide and chloride, and only in this form. According to the equation, more of the iodide (mol. wt. 502.55) than of the chloride (mol. wt. 226.5 × 2 = 453) should be obtained. The actual quantities weighed were 12.5 grams of antimonous iodide and about 11 grams of antimonous chloride. As compared with the theoretical amounts of the two substances which should have been expected from the materials of the four tubes, only about 85 per cent of the iodide and 80 per cent of the chloride were obtained. But it must be remembered that the antimony chloride used was only the commercial article, and the phosphonium iodide can never be prepared in a state approximating purity; and further, that in the scraping out of the substances from the tubes and the many operations involved in the treatment of the products of the reaction, considerable loss of the substance could not be avoided.

3. The amount of hydrochloric acid gas which escaped is really decisive in the interpretation of the reaction. Under the most favorable conditions, a tube which contained 3.6 grams of phosphonium iodide and 6.8 grams of antimonic chloride lost 2.4 grams from the escape of gases. The theoretical

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[1] J. P. Cooke : Proc. Am. Acad. of Arts and Sciences, [2], **5**, 72.

loss of hydrochloric acid and hydrogen phosphide, according to the equation, should have been 2.7 grams. The loss found amounted to 90 per cent of the one calculated. A better agreement could not be expected considering the condition of the materials used.

4. Red phosphorus was obtained in sufficient quantities to satisfy the theory, and the formation of phosphine gas, which was observed in the later stages, can be assumed to have proceeded in accordance with the equation.

As was mentioned above, the antimony triiodide which forms in the reaction was obtained in two modifications, in a red and in a yellow one. It is interesting to note that from one and the same benzene solution, on gradual concentration, there first separated out red crystals exclusively, then followed a crop of mostly yellow crystals, then again red ones, and lastly, antimonous chloride, which remained somewhat contaminated with the red antimonous iodide.

The reaction between antimonic chloride and phosphonium iodide is, it appears, essentially a reducing one. All the antimonic chloride is reduced to the antimonous state. When equal numbers of molecules of the two reagents are used, a third of the antimonous chloride is converted into antimonous iodide.

The reducing properties of phosphonium iodide are well known, but we are not aware that it has as yet been at all made use of in this capacity in inorganic chemistry. And yet it would appear from the reaction just described that it may become serviceable to the inorganic chemist.

According to H. Rose,[1] antimonic chloride and phosphine form an addition-product, some hydrochloric acid gas being evolved at the same time. But R. Mahn,[2] in repeating Rose's experiment, failed to obtain the addition-product in question. He found instead that the two bodies act upon one another according to this equation :

$$4SbCl_5 + PH_3 = 4SbCl_3 + PCl_5 + 3HCl.$$

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[1] Pogg. Ann., **24**, 165.

[2] Jenaische Ztschr. f. Medicin u. Naturwiss., **5**, 158.

II.

Action of Phosphonium Iodide on Phosphorus Pentachloride.

These two substances act upon one another even at ordinary temperatures, but the reaction does not seem to proceed much beyond the point of contact of the two bodies. When heated in a sealed tube they undergo the following reaction :

$$3PCl_5 + 3PH_4I = PI_3 + PCl_3 + 12HCl + P_4.$$

Not only is the pentachloride reduced to a lower halide, but a part of its phosphorus is also reduced to the elementary condition. In one experiment the formation of diphosphorus tetraiodide was observed, which probably resulted from a secondary reaction between the phosphorus triiodide and phosphorus.

The progress of the reaction seems to be very much influenced by the circumstance as to whether the two substances are thoroughly mixed with one another before the digestion or not. In the former case one can observe, as an intermediate stage, the formation at about 80° C., of a liquid from which, if allowed to cool, short, fine needles separate. If no mixing took place the intermediate formation of a liquid was not observed.

The following are some of the experiments made with phosphonium iodide and phosphorus pentachloride :

Two tubes, each containing 2 grams of phosphonium iodide (1 mol.) and 2.6 grams of phosphorus pentachloride (1 mol.) were sealed and heated two and one-half hours at 90° to 100°. On cooling, in only one tube was any liquid noticed. On opening, an acid, non-inflammable gas escaped—hydrochloric acid ; no phosphine, no hydriodic acid. The losses in weight were : (I.) 0.9 gram ; (II.) 1 gram. On further heating for three hours at 100° to 110°, again only hydrochloric acid escaped and to the following extent: From (I.) 0.5 gram, and from (II.) 0.65 gram. The tubes were now digested for five hours at 120° to 125°, upon which they lost 0.35 gram and 0.25 gram of hydrochloric acid, respectively. Further digestion did not cause the evolution of any more gas. The product was entirely solid, mostly red in color but to a small extent yellow.

In order to separate the phosphorus trichloride from the reaction-product in which it is present in but small quantity (theoretically to 2 grams of phosphonium iodide correspond 0.46 gram of the trichloride) we proceeded in one case as follows: The mass in the tube was treated with carbon disulphide which is said to dissolve freely both of the iodides of phosphorus as well as the trichloride of this element, and the solution distilled over a water-bath. For some reason or other no phosphorus trichloride (boiling-point 76°) was obtained.

The following method, however, proved successful for the separation of the trichloride: The tube containing the reaction-product was bent in the middle to almost a right angle, the tip sealed, and then the contents of the tube subjected to distillation. The lower half of the tube was immersed in boiling water while the upper half, with the tip, dipped into cold water. Recourse was had to distillation in a closed tube in order, by duplicating the conditions under which the reaction took place, to avoid possible interaction between the trichloride and the iodide of phosphorus. As a result of this distillation a sufficient quantity of a colorless liquid was obtained, to be easily identified as phosphorus trichloride. It became hot when a few drops of water were added to it, and the water solution so formed (phosphorous acid) reduced silver nitrate and mercuric chloride from their solutions.

Upon the removal of the phosphorus trichloride the contents of the tube were treated with carbon disulphide and the solution formed was filtered and concentrated, when short, red needles separated, which, by their melting-point of 55° C., were easily identified as phosphorus triiodide. The residue left after the treatment with carbon disulphide consisted of red phosphorus.

Conclusive evidence of the fact that the reaction between phosphonium iodide and pentachloride takes place as indicated by the equation given above, is supplied by the amount of hydrochloric acid liberated. The two tubes lost, respectively, 1.75 and 1.9 grams of hydrochloric acid. According to theory they should have lost 1.83 grams.

In one experiment in which the digestion was finished at a higher temperature (135°), some well-shaped crystals were found in the upper part of the tube. A melting-point was taken and proved to be 110°, which is the melting-point of diphosphorus tetraiodide, P_2I_4.

On the whole, it may be stated that the reaction between phosphorus pentachloride and phosphonium iodide is similar in nature to that between the latter and antimony pentachloride. In both cases the phosphonium iodide acts as a reducing agent, but in the case of phosphorus pentachloride the reduction is more complete, for not only is the phosphorus pentachloride reduced to phosphorus trichloride (in a part of which the chlorine is replaced by iodine), but one-third of it is reduced to elementary phosphorus.

According to Mahn,[1] hydrogen phosphide acts on phosphorus pentachloride according to the equation :

$$PH_3 + 3PCl_5 = 4PCl_3 + 3HCl.$$

III.

Action of Phosphonium Iodide on Tin Tetrachloride.

In the study of the action of phosphonium iodide upon tin tetrachloride, the previous elucidation of the reaction between phosphonium iodide and antimony pentachloride, and between the former and phosphorus pentachloride, was of great advantage. But for the experience so gained we might have been led to an imperfect interpretation of what takes place when tin tetrachloride and phosphonium iodide are heated in a closed tube, for the first experiments seemed to point to the following reaction :

$$4SnCl_4 + 4PH_4I = SnI_4 + 3SnCl_2 + 10HCl + 2PH_3 + P_2.$$

As a matter of fact, the tin tetraiodide was obtained in considerable quantity and identified by a complete quantitative analysis. Moreover, the amount of hydrochloric acid and phosphide seemed to accord with the equation. But on comparing this reaction with that taking place between phosphorus pentachloride and phosphonium iodide,

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[1] Jenaische Ztschr. f. Medicin u. Naturwiss., **5**, 158.

$$3SbCl_5 + 3PH_4I = SbI_3 + 2SbCl_3 + 9HCl + PH_3 + P_2,$$

we were struck by the relative incompleteness of the former. It appeared strange that the stannic iodide was not reduced to stannous iodide. The digestion was, therefore, continued for longer periods of time and at higher temperatures with the result that the reduction was as complete as that which takes place when antimony pentachloride is treated with phosphonium iodide. Thus the reaction is really as follows:

$$6SnCl_4 + 6PH_4I = 3SnCl_2 + 3SnI_2 + 18HCl + 2PH_3 + 4P.$$

When tin tetrachloride and phosphonium iodide are brought together at ordinary temperatures a mild reaction sets in, which stops after a short time if the access of moist air is prevented. A steady reaction between the two bodies begins in the neighborhood of 100° C.

The following are some of the experiments made with tin tetrachloride and phosphonium iodide. In the first experiments the tin tetrachloride, contained in a short tube of small bore, was placed in one of a larger bore into which the phosphonium iodide had previously been introduced. Four tubes, each containing 6.5 grams (3 cc.) of tin tetrachloride (1 mol.), and 4 grams of phosphonium iodide (1. mol.) were digested four hours between 90° and 100° C. On cooling, a thin, orange-yellow sublimate, covering the whole inner surface of the tube, was to be observed. The most of the phosphonium iodide lay unchanged at the lower part of the tube and above it a black mass was formed. Only one tube (I.) was opened. Four-tenths gram of a non-inflammable acid escaped, which proved to consist of pure hydrochloric acid. On further treating for twelve hours at 112° to 115° C. the tube, which had lost 0.4 gram of hydrochloric acid, lost 0.5 gram more of the same gas. After heating for one-half hour longer at 120° to 125° tube II. gave off, on cooling, 1 gram and tube III. 0.9 gram of hydrochloric acid not contaminated with either hydriodic acid or phosphine. Tube I. was not opened this time. One tube exploded. Further digesting for three and one-half hours at 120° to 125° caused the following losses of pure hydrochloric acid : Tube I. 0.8 gram, tube II. 0.7 gram, tube III. 0.6 gram. The sublimate inside the tube was orange-red. On continued heating for one and one-half hours at 125° to 135°, the losses were, I. 0.4 gram, II. 0.45 gram, III. 0.45 gram. The escaping gases became inflamed for an instant. The presence of phosphine in the issuing gases was further proved by the silver nitrate test. On addition of the latter reagent to a solution of a part of the liberated gases in water a dark precipitate was found. This precipitate, with the exception of some minute black specks (silver phosphide), redissolved immediately on the addition of ammonia. The black specks redissolved only on vigorous shaking. Some unchanged phosphonium iodide was still to be seen at the lower part of the tube. On further digestion for three hours at 130° to 135° the losses were, I. 0.25 gram, II. 0.25 gram, III. 0.3 gram. The opening of the tubes was accompanied by a sharp noise, the escaping gases burning for a few seconds. The heating was now still further continued for seven hours at 130° to 135° with the result that tube I. lost 0.2 gram, tube II. 0.3 gram, tube III. 0.3 gram of hydrochloric acid and phosphine. The tubes were digested once more, this time for six hours, up to 160°. Only 0.1 gram of gas escaped from each tube, the outflowing gases burning for some time. The reaction was considered as finished. The total losses of the three tubes were, I. 2.65 grams, II. 2.65 grams, III. 2.8 grams.

The reaction-product was removed from the tubes and digested repeatedly with benzene by the aid of a reflux condenser. On concentrating the benzene solution by distillation, a crop of red crystals was obtained which proved to be stannic iodide. This was identified by its melting-point (146° C.) and by analysis.

I. 0.2156 gram substance gave 0.0526 gram SnO_2, corresponding to 0.04138 gram tin.

II. 0.3444 gram substance gave 0.5162 gram AgI, corresponding to 0.2789 gram iodine.

	Calculated for SnI_4.	Found.
Sn	19.01	19.19
I	80.99	80.98

The residue, after extraction with benzene, could be expected to contain stannous chloride, free phosphorus, and perhaps stannous iodide also. Since absolute alcohol is said to dissolve stannous chloride without decomposition while stannous iodide is not known to be soluble in this medium, it was hoped, by treating the residue with absolute alcohol, to separate the stannous chloride. The attempt, however, was a failure. On heating the residue with absolute alcohol a light-red solution was obtained which contained both a chloride and an iodide. The solution soon became much darker in color, and when tested with hydrogen sulphide in the usual way, gave a bright-yellow precipitate, showing, consequently, the presence of a large quantity of a stannic compound. This was perplexing. On concentrating the solution almost all the alcohol had to be evaporated before solidification of the dissolved substance took place. The solid mass was dark-yellow and more or less resinous. It was transferred to a distilling-flask and subjected to a gradually increasing heat. At first some highly-colored alcohol went over; then, upon applying the naked flame directly to the distilling-flask, a slightly-colored, fuming liquid followed, and soon dry, porous, black lumps were seen to form in the distilling-flask. The fuming liquid was tin tetrachloride and the black mass more or less pure tin. It is a well-known characteristic of stannous chloride to break up into stannic chloride and tin.

The following appeared to be shown by the experiments just described: (1) Stannic iodide was present in considerable quantity in the reaction-product, (2) stannous chloride was undoubtedly proved to be a part of the latter, (3) red phosphorus (which remained after the residue obtained upon the removal of the stannic iodide was treated with alcohol) was one of the products of the reaction, and (4) a certain amount of hydrochloric acid and phosphine were evolved. Guided especially by the quantity of gases evolved, the following equation appeared to represent the reaction which took place :

$$4SnCl_4 + 4PH_4I = SnI_4 + 3SnCl_2 + 10HCl + 2PH_3 + P_2.$$

According to this equation a loss of 2.7 grams of hydrochloric acid and phosphine would correspond to 4 grams of phosphonium iodide (with its equivalent quantity of tin tetrachloride) while in the three tubes described above there were lost respectively, 2.65 grams, 2.65 grams, and 2.8 grams.

As was discussed above, the strange thing about such a reaction would be that stannic iodide should remain unreduced. In order to clear up this apparent anomaly another series of experiments was carried through.

Two tubes were filled as before with 6.5 grams of tin tetrachloride and 4 grams of phosphonium iodide, but this time no small tube was used to keep the two substances apart. While filling the digestion-tube in this case it was kept surrounded by a mixture of salt and ice, for we had found that at the temperature of a freezing-mixture phosphonium iodide and tin tetrachloride do not act upon one another in the slightest. As a result of this method of filling the tubes, not only is the reaction considerably accelerated owing to the mixing of the substances directly, but the direct mixing is probably necessary for the complete reaction. In the latter period of the digestion the resulting mass is very compact, and thorough mixing, as well as free communication throughout the tube, appears to be a great advantage. The presence of a small tube inside the larger is certainly an impediment in this case.

But even with the freely mixed substances the reaction was slow. After digesting for a long time, during which the tubes were opened from time to time, and the temperature raised toward the end to from 160° to 170°, a total loss of 2.95 grams and 3.05 grams, respectively, was noted. Having kept the tubes for a couple of hours at 160° to 170°, and having observed a loss of only 0.1 gram in each case, the reaction was therefore considered as completed.

The contents of one tube (loss 3.05 grams) was treated repeatedly with carbon disulphide in which tin tetraiodide is said to be very soluble, but on concentrating the filtrate very little tin tetraiodide was found. It occurred to us that it might be advisable to digest the phosphonium iodide and tin tetrachloride at a still higher temperature. The remaining tube was therefore heated for some hours at 250° to 260°, upon which an additional loss of 0.2 gram was observed (total loss 3.15 grams). In this tube scarcely any tin tetraiodide could be detected, after repeated digestion with benzene under the reflux condenser. Having settled the question as to the absence of tin tetraiodide, it remained only to identify the stannous chloride and iodide. The presence of stannous compounds was demonstrated by tests presently to be described.

The residue, after treatment with benzene, was dried and shaken up with water, from which the air was removed by boiling, and the liquid filtered. The first part of the filtrate, as it came through, appeared to be clear, but soon the whole filtrate became turbid. A portion of the filtrate clarified by a couple of drops of hydrochloric acid, gave the characteristic dark-brown precipitate of stannous sulphide. Another portion of the filtrate, acidified with hydrochloric acid, was added to a solution of mercuric chloride—a cinnabar-red precipitate was formed which, upon further addition of the filtrate and warming, turned into metallic mercury. An ammoniacal solution of silver nitrate was also reduced by the filtrate.

In order to demonstrate that both iodine and chlorine were present in the filtrate a portion of the latter, acidified with tartaric acid, was treated with hydrogen sulphide, the dark-brown precipitate filtered off, and the filtrate heated to drive off the hydrogen sulphide. On addition of silver nitrate to this filtrate a light-yellow precipitate was formed which only partly redissolved in ammonia. On filtering off the precipitate and neutralizing the filtrate with nitric acid, a white precipitate of silver chloride separated.

It appears from the above tests that the presence of stannous chloride and stannous iodide in the reaction-product is unmistakably proved.

If in the products of the reaction between tin tetrachloride and phosphonium iodide stannic iodide is absent, then the reaction has to be represented by the following equation :

$$6SnCl_4 + 6PH_4I = 3SnCl_2 + 3SnI_2 + 18HCl + 2PH_3 + 4P.$$

Strongly corroborative of this equation is the consideration of the amount of gases set free in the reaction. In the tubes which were digested under the most favorable circumstances the loss of the escaping gases was respectively 3.05 and 3.15 grams. According to this last equation the loss should be 3.3 grams.

The study of the reaction between phosphonium iodide and tin tetrachloride shows that the former is just as effective in reducing the latter as it was in reducing antimonic chloride.

The study seems, moreover, to afford some insight into the successive steps by which the final reduction of tin tetrachloride is gradually accomplished. The formation of stannous iodide results, at least in part, from the reduction of the stannic iodide previously formed.

The action of phosphoretted hydrogen upon stannic chloride was studied by H. Rose[1] and R. Mahn.[2] According to the former, tin tetrachloride absorbs hydrogen phosphide and gives a yellow solid, which fumes in the air. Mahn, by distilling this addition-product in a current of carbon dioxide, got rid of the unchanged tin tetrachloride, to which the fuming was due, and obtained a non-fuming, dark powder. A series of discordant analyses of this powder led him to the formula $Sn_3Cl_6P_2$.

Contributions from the Chemical Laboratory of Union College.

CERTAIN SUBSTITUTION DERIVATIVES OF ETHYL ANILINOMALONATE.

BY RICHARD SYDNEY CURTISS.

In two previous papers[3] I described a compound produced by the action of nitrous acid on ethyl anilinomalonate,

$$C_6H_5NH.CH(CO_2C_2H_5)_2.$$

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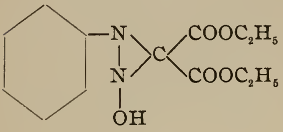
[1] Pogg. Ann., **24**, 159.

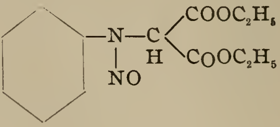
[2] Jenaische Ztschr. f. Medicin u. Naturwiss., **5**, 158.

[3] This JOURNAL, **23**, 509; **28**, 315.

Sodium and potassium hydroxides react with this compound to form well-defined salts. It gives Liebermann's nitroso reaction (contrary to a former erroneous statement),[1] while its alcoholic solution reacts but slowly with ferric chloride, producing a dull-red color. The substance is either ethyl phenyloxydiazomalonate[2] (I.) or ethyl nitrosoanilinomalonate (II.), or perhaps a mixture of the two tautomeric compounds:



I.



II.

As the substance decomposes easily when brought into contact with reagents, and gives nitrogen and its oxides, the corresponding ortho-, meta-, and para-substituted methyl derivatives have been made, with the idea that some of these might have a greater stability of the nitrogen chain, thereby rendering more easy the study of their structure as acids, or pseudo-acids.

In order to prepare these compounds it was first necessary to make the ortho-, meta-, and paratoluidinomalonates. These were formed from ethyl brommalonate (b. p. 120° to 125° under 14 mm. pressure) and Kahlbaum's pure toluidines, by the general method already given[3] for making ethyl anilinomalonate.

The ethyl ortho-, meta-, and paratoluidinomalonates are weak bases. Their salts with the strong mineral acids are decomposed by water, the base usually separating in the form of an oil. When treated with nitrous acid they yield thick, amber-colored oils. When treated with sodium or potassium hydroxides these amber oils give yellow solutions, or stable, yellow, crystalline salts. They also give Liebermann's nitrosamine test, and react slowly with ferric chloride solution, forming deep-red colors.

[1] This JOURNAL, **23**, 510.

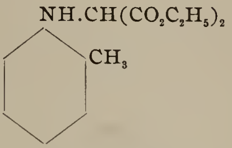
[2] *Ibid.*, **28**, 315. Incorrectly printed as ethyl α-phenyloxydiazomalonate.

[3] *Ibid.*, **19**, 693.

In describing the compounds formed by the action of nitrous acids on these bases, they will, for convenience, be spoken of at present as nitrosamines. Their possible tautomeric structure, as substituted ethyl phenyloxydiazomalonates (I.) will be considered in a later paper on this subject.

EXPERIMENTAL PART.

Ethyl Orthotoluidinomalonate,



.—To prepare this substance 50 grams of ethyl brommalonate (1 molecule) are mixed with 60 grams of orthotoluidine ($2\frac{2}{3}$ molecules). If the mixture is allowed to stand several days it gradually darkens and a crystalline mass separates. It is better, however, to heat it on the water-bath at 100°. This causes the clear liquid to darken and the separation of orthotoluidine hydrobromide begins in a few minutes. The reaction is complete in one or two hours.

The crystal mass is filtered and washed with ether, with the aid of a pump. The magenta-colored filtrate is then washed with a slight excess of dilute hydrochloric acid, to remove the unchanged base, as well as the colored impurities. The ethereal solution, when dried over calcium chloride and the ether distilled off, leaves a clear, reddish-yellow oil (the yield is 92 per cent of the theory). This product was freed from ethyl brommalonate and other impurities, by treatment with hydrochloric acid gas, as described below. This forms a salt with the base. To regenerate the base from the purified hydrochloride it is only necessary to shake the latter with water and ether. The ethereal solution is then thoroughly washed with water to neutral reaction and dried over calcium chloride. When the ether is distilled off in a vacuum a nearly colorless oil is left which slowly reddens on standing several days in the light. The base thus purified and dried over sulphuric acid was used in the following analysis :

0.2630 gram substance gave 0.6094 gram CO_2 and 0.1726 gram H_2O.

0.2743 gram substance gave 12.9 cc. N at 14° and 750.3 mm.

	Calculated for $CH_3.C_6H_4.NH.CH(CO_2C_2H_5)_2$.	Found.
C	63.33	63.16
H	7.22	7.34
N	5.30	5.51

It is easily soluble in benzene, acetone, chloroform, ether, alcohol, and ligroin. It slowly reduces an ammoniacal silver nitrate solution, forming a bright mirror, and an alkaline solution of potassium permanganate is instantly decolorized. It dissolves in concentrated hydrochloric and sulphuric acids, and is reprecipitated from these solutions by adding an equal volume of water. Concentrated nitric acid forms with it, on standing, a yellow, crystalline product, soluble in ether and insoluble in water. When the oil is heated to the point of distillation, decomposition is effected, gases are evolved, and on cooling a light-green, crystalline compound appears, which melts at about 140°, and is soluble in a solution of sodium hydroxide. This change will be further studied.

Ethyl Orthotoluidinomalonate Hydrochloride.—A solution is made of the above-mentioned base, in an equal volume of ether, and dry hydrochloric acid gas is passed into it until the reaction is complete. The resulting dark-red solution may be quickly changed to a crystalline mass by rubbing with a glass rod. Inasmuch as this salt, even when pure, fumes in the open air, and is rapidly decomposed by moisture, it is best purified when washed with dry toluene by decantation, rather than on the filter.

The salt, when dried in a vacuum over sulphuric acid, was analyzed.

0.3018 gram substance gave 0.1440 gram AgCl.

	Calculated for $CH_3.C_6H_4.NH(HCl).CH(CO_2C_2H_5)_2$.	Found.
Cl	11.76	11.80

Prepared as above, it is a white, or pink-white, crystalline substance, which melts at 87° to 90°. It may be kept in the dark over sulphuric acid for months, but when exposed to light it quickly turns to a magenta color. It dissolves readily in acetone and chloroform, is fairly soluble in alcohol, and slightly so in ether, toluene, benzene, and carbon tetrachloride, and is easily decomposed by water into hydrochloric acid and the original base, as stated above.

Ethyl Nitrosoorthotoluidinomalonate.—This substance may be made either from the free base in acid solution, or from the hydrochloride itself, prepared as above.

Forty and one-tenth grams of the hydrochloride are mixed with 50 cc. of water, which liberates the base as an oil. To this 9.5 grams of pure sodium nitrite (0.3 gram excess) dissolved in 25 cc. of water, are slowly added. The mixture is constantly shaken in a well-stoppered bottle and kept below 15°. The absorption of nitrous acid is complete and the operation is finished in twenty minutes. After the bottle containing the oily emulsion has stood in cold water three-quarters of an hour, the mixture is extracted with ether. The latter is washed thoroughly, first with cold water, then with a little sodium carbonate solution, and lastly, many times with cold water. This golden-yellow ethereal solution, dried over calcium chloride and evaporated in a vacuum, leaves 37.5 grams of an oil. This could neither be crystallized nor distilled. The substance yields well-defined alkali salts,[1] and for its purification it was regenerated from one of these.

Regeneration of Ethyl Nitrosoorthotoluidinomalonate from its Sodium Salt.—Five grams of the pure, finely-powdered salt are partly dissolved in 25 cc. of cold water, and to this 25 cc. of ether are added. A rapid stream of carbon dioxide is passed through the liquids, which are kept cold by immersing the flask in ice-water. The yellow color of the aqueous solution gradually passes into the colorless ether as the decomposition goes on. In twenty to thirty minutes, when the water has become colorless, which fact indicates the end of the reaction, the ether is separated and washed with cold water to neutral reaction. It is then dried over calcium chloride.

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[1] The preparation and properties of these alkali salts will be described in a later paper.

While evaporating the ether off in a vacuum-desiccator, light-colored crystals formed in small quantity on the sides of the cold dish. These soon melted at the temperature of the room, and could not be obtained again even when the oil stood for a long time at a very low temperature. The above product is a clear oil of a slight reddish tint, has the consistency of honey, is nearly odorless, and could not be crystallized. It undergoes no change on being kept in a desiccator, over sulphuric acid, for six weeks. The yield is 3.8 grams. It was dried over sulphuric acid for five or six days and analyzed.

0.3023 gram substance gave 0.6299 gram CO_2 and 0.1697 gram H_2O.

0.2061 gram substance gave 17.2 cc. N at 15° and 754.5 mm. pressure.

	Calculated for $CH_3.C_6H_4.N.(NO).CH.(CO_2C_2H_5)_2$.	Found.
C	57.08	56.79
H	6.17	6.28
N	9.55	9.80

The substance thus purified gives the Liebermann nitroso reaction. Its alcoholic solution is changed by ferric chloride to a dull-red color, which does not appear immediately, however, but becomes faintly apparent only after three or four seconds have elapsed, and then darkens slowly. It dissolves easily in chloroform, carbon tetrachloride, benzene, acetone, and ethyl acetate, is fairly soluble in alcohol and ether, and slightly so in ligroin. It is insoluble in cold water, but dissolves sparingly in hot. A solution of sodium carbonate dissolves it slightly and assumes a yellow color. Concentrated solutions of sodium and potassium hydroxides form immediate precipitates of well-crystallized salts, from which the original oil may be regenerated by mineral acids, or even by carbonic acid, as described above.

Ethyl Metatoluidinomalonate.—Twenty-four grams of ethyl brommalonate were mixed with 21.4 grams of metatoluidine (about 3 molecules). After standing at ordinary temperatures for two hours, crystals of toluidine hydrobromide begin to separate. The reaction is hastened by heating the mixture from forty to sixty minutes at 100°, on the water-bath. This completes the reaction, and causes the crystalline mass to turn green if longer continued. After cooling, the dissolved hydrochloride is precipitated from the thick, dark liquid by the addition of three or four volumes of ether, and is then filtered off on the pump. The yield is 85 to 95 per cent of the theory.

The red, ethereal solution is then worked up as described above, in the preparation of ethyl orthotoluidinomalonate. When it is brought to that stage of the process, where the ether is evaporated, the new compound slowly crystallizes out as a dark mass of rosettes of prismatic needles. This is then freed from the oily mother-liquor by suction with a filter-pump, and washed thoroughly with ligroin. The product is 21 grams of lavender-white crystals. This is purified for analysis by recrystallization from ligroin or absolute alcohol. Thus prepared, it forms colorless needles. It melts at 50°.5 to 51°, forming a clear liquid which does not change when heated to 200°. From 220° to 250° gases are given off, and, after cooling, a new crystalline mass appears. This product will also be further studied.

The analysis of the pure base (m. p. 50°.5 to 51°) follows :

0.2070 gram substance gave 0.4819 gram CO_2 and 0.1331 gram H_2O.

0.3206 gram substance gave 15.2 cc. N at 16°.5 and 732.1 mm.

	Calculated for $CH_3.C_6H_4.NH.CH(CO_2C_2H_5)_2$.	Found.
C	63.33	63.45
H	7.22	7.19
N	5.30	5.37

The substance dissolves easily in ether, chloroform, acetone, toluene, and benzene, is slightly soluble in alcohol, dissolves very easily in hot ligroin, but is nearly insoluble in the cold solvent. Concentrated hydrochloric acid dissolves it, but it is reprecipitated as an oil on the addition of much water to this solution. It rapidly reduces an alkaline solution of potassium permanganate. Ammoniacal silver nitrate is reduced slowly, forming a dark deposit of silver.

Ethyl Metatoluidinomalonate Hydrochloride.—When dry hydrochloric acid gas is passed, to saturation, through an ethereal solution of ethyl metatoluidinomalonate, and the ether and excess of acid are evaporated over sulphuric acid, a thick, colorless oil is left. By rubbing this with a little ligroin, at a low temperature, the oil is with difficulty made to crystallize. After a crystal has been once obtained, however, and a minute particle is thrown into the oil, it solidifies quickly. This crystalline mass was washed entirely by decantation, first with dry ligroin, then with ligroin-benzene, and allowed to stand in a vacuum over sulphuric acid for two or three weeks. It was then analyzed:

0.4040 gram salt gave 0.1871 gram AgCl.

	Calculated for $CH_3.C_6H_4.NH(HCl).CH(CO_2C_2H_5)_2$.	Found.
Cl	11.76	11.45

The salt crystallizes from its solutions in alcohol or ether in beautiful rosettes of white, silky needles. It is easily soluble in chloroform, benzene, acetone, ethyl acetate, and alcohol; fairly so in ether and toluene; slightly so in carbon tetrachloride and ligroin. It melts at 80° to 83°, forming a clear liquid.

Ethyl Nitrosometatoluidinomalonate.—This substance can best be prepared according to the following method: 13.3 grams of the pure crystals of ethyl metatoluidinomalonate are finely pulverized and mixed with 2.5 grams (0.1 gram excess) of real sulphuric acid in 27 cc. of water. To this 3.9 grams (0.4 gram excess) of pure sodium nitrite, in 40 cc. of water, are slowly added with constant shaking. The temperature of the mixture should be kept below 15°. The reaction begins immediately. The white powder in suspension in the water at first turns yellow, then soon becomes packed into an oily ball. To increase the surface exposed to action a little ether is added which dissolves both the amine and its reaction-product. The agitation of the mixture is continued for ten to fifteen minutes after the addition of the nitrite is complete. The ether is then separated from the yellow aqueous solution and washed once with water, then with a solution of sodium carbonate to alkaline reaction, and finally very thoroughly with cold water. This ethereal solution, after being dried over calcium chloride, is evaporated down on the water-bath, the last portions of ether being removed in a vacuum-desiccator over sulphuric acid. During this process crystals separate out. The dry crystalline mass is washed with ether with the aid of a filter-pump. The filtrate is colored a deep strawberry-red, while the crystals themselves have a faint reddish-yellow color. The yield was 9.1 grams.

From the mother-liquor and washings, 3.4 grams more of deep-red crystals were obtained. The total yield was nearly quantitative. The substance is best purified by recrystallization from hot ligroin (b. p. 60° to 80°). On cooling a hot saturated solution it separates, at first, as an oil. However, by slow and careful cooling, while rubbing with a glass rod, it can be made to separate in a pure crystalline form. This product, filtered and well washed with cold ligroin, dried in a vacuum over sulphuric acid, and analyzed, gave the following figures:

0.2229 gram substance gave 0.4652 gram CO_2 and 0.1244 gram H_2O.

0.1986 gram substance gave 16.4 cc. N at 19°.2 and 755.4 mm.

	Calculated for $CH_3.C_6H_4.N.(NO).CH(CO_2C_2H_5)_2$.	Found.
C	57.08	56.89
H	6.17	6.24
N	9.55	9.56

Thus purified the substance consists of beautiful, transparent, pinkish-amber prisms[1] (apparently monoclinic), which melt at 58° to 58°.5, forming a clear liquid. If the heating be continued above its melting-point, gases are evolved from 125° to 200°. At 220° the color darkens. If cooled at this point a crystalline body is obtained, which melts at 126° to 127°. This new substance is fairly soluble in alcohol and in ether and does not give the nitrosamine test of Liebermann.

[1] The pink color is no doubt due to very slight traces of a decomposition-product which cannot be completely removed by repeated recrystallization, inasmuch as attempts to decolorize it, by boiling its alcoholic solution with pure bone-black, resulted in the formation of larger quantities of this brilliant orange-red impurity.

Ethyl nitrosometatoluidinomalonate becomes highly electrified on rubbing with a glass rod. It dissolves readily in benzene, toluene, xylene, ethyl acetate, acetone, and glacial acetic acid; is fairly soluble in ether and alcohol; only slightly so in cold ligroin, but dissolves easily when the ligroin is hot. Cold solutions of sodium carbonate and sodium hydroxide act slowly on the body, as it is insoluble in water. If, however, these solutions are warmed to the melting-point of the crystals it dissolves fairly well. On neutralizing the resulting yellow solutions with dilute hydrochloric acid the nitrosamine is regenerated and appears as a white, oily emulsion.

The crystalline body gives Liebermann's nitrosamine test. Ferric chloride added to a dilute alcoholic solution of the crystals, turns it, at first, straw-yellow, then, after a few seconds, it begins to redden and gradually assumes a dark, brownish-red color in thirty to sixty seconds.

Ethyl Paratoluidinomalonate.—This compound has already been described briefly by Blank,[1] and has the solubilities ascribed to it by him. I have made it in large quantities by the general method described above in making the analogous bases, and note here the following additional properties.

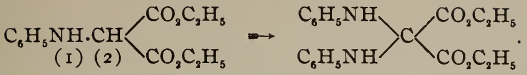
It is a weak base like the ortho- and meta-isomers. It dissolves in concentrated hydrochloric and sulphuric acids and is reprecipitated, by addition of water, as an oil which soon crystallizes. Cold nitric acid, acting on it, appears to form a yellow compound soluble in ether.

Its alcoholic solution slowly reduces a hot, ammoniacal, silver nitrate solution to metallic silver, and an alkaline solution of potassium permanganate is instantly decolorized by it.

The behavior of these substituted ethyl anilinomalonates with weak oxidizing agents is of interest, inasmuch as it has been shown[2] that ethylanilinomalonate itself, simply by being oxidized with mercuric oxide or potassium permanganate, in ligroin solution, undergoes a peculiar reaction, by which it is changed to ethyl dianilinomalonate.

[1] Ber. d. chem. Ges., **31**, 1815.

[2] Curtiss: This Journal, **19**, 694.



$$\underset{(1)\ (2)}{C_6H_5NH.CH}\left<\begin{matrix}CO_2C_2H_5\\CO_2C_2H_5\end{matrix}\right. \longrightarrow \left.\begin{matrix}C_6H_5NH\\C_6H_5NH\end{matrix}\right>C\left<\begin{matrix}CO_2C_2H_5\\CO_2C_2H_5\end{matrix}\right..$$

It is of interest to note, however, that recent experiments have shown that no such transformation results if a little calcium chloride powder is added to the ligroin solution to hold the water which may be formed by the oxidation of the two very reactive hydrogen atoms (1 and 2).

Ethyl Nitrosoparatoluidinomalonate.—To make this compound, 4.7 grams of finely powdered ethyl paratoluidinomalonate are dissolved in a little ether and mixed with 0.95 gram of sulphuric acid in 20 cc. of water. To this, in a well-stoppered bottle, is slowly added a solution of 1.3 grams of pure sodium nitrite in 20 cc. of water. The reaction proceeds under the same general conditions as already described in similar cases, and is complete in thirty to forty minutes. After washing the ethereal solution well with a solution of sodium carbonate, and with water, drying it over calcium chloride, and removing the ether in a vacuum, a clear amber oil remains.

It is purified by regenerating it from its pure sodium salt by means of carbon dioxide, as described above in the purification of ethyl nitrosoorthotoluidinomalonate. It was prepared in this way, dried over sulphuric acid, and analyzed :

0.2986 gram substance gave 0.6230 gram CO_2 and 0.1645 gram H_2O.

0.2719 gram substance gave 22.2 cc. of N at 15° and 746 mm.

	Calculated for $CH_3.C_6H_4.N.(NO).CH(CO_2C_2H_5)_2$.	Found.
C	57.08	56.87
H	6.17	6.16
N	9.55	9.48

The substance is a clear, greenish-yellow oil of honey-like consistency, which gradually turns slightly red while standing two or three weeks in the desiccator over sulphuric acid. It could be obtained in the crystal form only with the greatest difficulty. On allowing a bit of the oil, in a little ligroin, to stand for a long time at —15°, with occasional rubbing with a glass rod, a few minute crystals were obtained. When one of these was placed in the main lot of oil and left for twenty-four hours at —15°, the latter slowly and only partially crystallized in short, monoclinic prisms. These were mostly lost in attempting to wash them free of the oily mother-liquor, as they are very soluble in all of the ordinary organic solvents. The few crystals remaining gradually liquefied with slight decomposition on standing ten days in the desiccator. The oil, as soon as obtained from its sodium salt, gives the Liebermann nitroso reaction. A ferric chloride solution acting on its alcoholic solution produces no immediate color, but after two or three seconds a faint red color appears, which gradually grows darker for twenty or thirty seconds. It is soluble in solutions of sodium and potassium hydroxide, and if the latter are concentrated, crystalline yellow salts are immediately precipitated.

The oil dissolves easily in ligroin, benzene, toluene, ether, chloroform, alcohol, and ethyl acetate, and is fairly soluble in carbon tetrachloride. It is insoluble in cold water.

The study of these compounds will be continued, and with special reference to the salt-forming properties and general behavior as acids, or pseudo acids, of those described here under the name of nitrosamines.

In closing I wish to express my thanks to Mr. Thomas G. Delbridge, instructor in this laboratory, to whom I am indebted for the above series of carefully conducted combustions.

UNION COLLEGE, SCHENECTADY, N. Y.,
March 16, 1903.

Contributions from the Sheffield Laboratory of Yale University.

CVI.—ON THE DOUBLE AND TRIPLE THIOCYANATES OF CAESIUM, CADMIUM, AND SILVER.

BY H. L. WELLS.

The compounds to be described are as follows :

Double Salts.

$CsCd(SCN)_3$;
$Cs_4Cd(SCN)_6.2H_2O$;
$CdAg_2(SCN)_4.2H_2O$.

Triple Salts.

$Cs_2CdAg_2(SCN)_6.2H_2O$;
$Cs_2CdAg_2(SCN)_6$;
$Cs_2CdAg_4(SCN)_8.2H_2O$;
$Cs_4Cd_3Ag_{10}(SCN)_{20}.6H_2O$.

To make a complete list of the compounds formed by the three simple salts under consideration, the following caesium-silver thiocyanates which have been described previously[1] should be mentioned:

$Cs_3Ag(SCN)_4$;
$Cs_2Ag(SCN)_3$;
and $CsAg(SCN)_2$.

The compound $CsCd(SCN)_3$ corresponds to $CsHg(SCN)_3$, as might be expected from the somewhat close relation of cadmium and mercuric compounds in general, but it is noticeable that there is no caesium-cadmium thiocyanate analogous to $Cs_2Hg(SCN)_4.H_2O$ or $Cs_2Zn(SCN)_4.2H_2O$, the latter being the only caesium-zinc salt which could be prepared.

The salt $Cs_4Cd(SCN)_6.2H_2O$ is rather remarkable from the fact that there is no mercuric or zinc double thiocyanate corresponding to it. It agrees, however, with $Cs_4Mn(SCN)_6$, except that it contains water. These 4 : 1 thiocyanates (leaving water out of consideration) belong to a type which is well-known among the double halides, as is shown by the following list, in which the cadmium salts are prominent:

$(NH_4)_4ZnCl_6$;
$(NH_4)_4CdCl_6$;
$(NH_4)_4CdBr_6$;
K_4CdCl_6;
K_4CdBr_6;
Cs_4PbCl_6;
Cs_4PbBr_6;
$(NH_4)_4SnCl_6.3H_2O$;
$K_4SnCl_6.3H_2O$.

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[1] This JOURNAL, 28, 263.

The salt $CdAg_2(SCN)_4.H_2O$ differs from $ZnAg_2(SCN)_4$ in containing a molecule of water of crystallization.

The triple salts $Cs_2CdAg_2(SCN)_6$ and $Cs_2CdAg_2(SCN)_6.2H_2O$ might be regarded as possibly derived from the double salt $Cs_4Cd(SCN)_6.2H_2O$, but it must be borne in mind that there is no apparent connection between most of the other types of triple thiocyanates[1] and the known double salts. The hydrous triple salt just mentioned belongs to the most extensive series of triple thiocyanates which has as yet been prepared. A list of them follows :

$Cs_2CaAg_2(SCN)_6.2H_2O$;
$Cs_2MgAg_2(SCN)_6.2H_2O$;
$Cs_2MnAg_2(SCN)_6.2H_2O$;
$Cs_2NiAg_2(SCN)_6.2H_2O$;
$Cs_2NiCu_2(SCN)_6.2H_2O$;
$Cs_2CoAg_2(SCN)_6.2H_2O$;
and $Cs_2CdAg_2(SCN)_6.2H_2O$.

The anhydrous triple salt $Cs_2CdAg_2(SCN)_6$, which is much more readily formed than the corresponding hydrous compound, is interesting, since it shows that water of crystallization is not essential to this general type of triple salts. It is evident, therefore, that water may be left out of consideration, in this case at least, in comparing the different types of these salts. This argument strengthens the view advanced in the previous communication,[2] that water does not appear to replace other constituents in passing from one type to another of triple thiocyanates.

The triple salts

$$Cs_2CdAg_4(SCN)_8.2H_2O \quad \text{and} \quad Cs_4Cd_3Ag_{10}(SCN)_{20}.6H_2O$$

represent new types. These two salts are not far apart in chemical composition, but they show distinct crystalline forms, as far as one habit of the first salt is concerned, but this has another habit of crystallization which closely resembles the second salt. A careful consideration of the analyses shows that the second salt, which is formed in the presence of an excess of cadmium thiocyanate, does not differ from the first salt simply in containing more cadmium thiocyanate, for the ratios of Ag to SCN are very close to 1 : 2 in both products, a condition which would be modified by simply varying cadmium thiocyanate. It seems possible, perhaps, that the salt with the complicated formula may be due to the crystallization of the first salt, $Cs_2CdAg_4(SCN)_8.2H_2O$, with an undiscovered, isomorphous salt, $CsCdAg_3(SCN)_6.2H_2O$. It will be seen in the experimental part that a slight indication of the existence of the latter compound has been obtained. If it does exist, it is also a new type.

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[1] This JOURNAL, 28, 245.
[2] *Ibid.*, 28, 254.

The entire lack of agreement between the triple thiocyanates of cadmium and those of zinc is very remarkable in view of the resemblance of many compounds of these two metals. This unexpected lack of correspondence appears to be in harmony with the disagreement of the double thiocyanates which has already been pointed out. For the sake of comparison, the formulas of the triple salts containing zinc and cadmium are here placed side by side :

$CsZnAg(SCN)_4.H_2O$;	
$Cs_2ZnAg(SCN)_5$;	
	$Cs_2CdAg_2(SCN)_6$;
	$Cs_2CdAg_2(SCN)_6.2H_2O$;
$CsZn_2Ag_3(SCN)_8$;	
$CsZn_2Ag_4(SCN)_9$;	
	$Cs_2CdAg_4(SCN)_8.2H_2O$;
	$Cs_4Cd_3Ag_{10}(SCN)_{20}.6H_2O$.

There are eight types of triple thiocyanates in the above table, and all but one of the salts are unique in their types. The two other types known at present are represented by four salts corresponding to $Cs_3BaAg_2(SCN)_7$ and the single salt $K_4BaAg_2(SCN)_8.H_2O$.

EXPERIMENTAL PART.

The cadmium thiocyanate used for this work was prepared by making an exact precipitation with barium thiocyanate and cadmium sulphate in dilute solution, filtering, and evaporating to crystallization. The salt is sparingly soluble and crystallizes without water, as stated by Meitzendorff.[1]

1 : 1 Caesium-Cadmium Thiocyanate, $CsCd(SCN)_3$.—This salt forms large crystals which are sometimes tabular, and again prismatic in habit. They are colorless and either transparent or frequently somewhat white and not fully transparent. The substance is stable in the air. It melts at 212° to 214°. The compound is formed under a wide range of conditions, for instance, when caesium and cadmium thiocyanates are mixed in the molecular proportions 8 : 1, 1 : 1, and 1 : 4 in aqueous solution and properly concentrated. In the case of the first proportion mentioned, the solution should not be concentrated too far, for then the 4 : 1 salt, to be described next, would be deposited. The volume should be about 100 cc. for 75 grams of caesium thiocyanate and 12 grams of cadmium thiocyanate. When 4 molecules of cadmium thiocyanate to 1 of the caesium salt are present in a solution, cadmium thiocyanate is usually deposited with the double salt. The salt can be recrystallized from water.

The following analyses were made of different crops:

	Calculated for $CsCd(SCN)_3$.	Found. I.	II.	III.	IV.	V.
Cs	31.71	....	....	....	....	....
Cd	26.80	26.85	26.80	....	....	27.46
SCN	41.49	41.10	41.59	41.41	41.19	41.91

4 : 1 Caesium-Cadmium Thiocyanate, $Cs_4Cd(SCN)_6.2H_2O$.—This salt forms large, nearly square, tabular crystals which are transparent, colorless, and stable in the air. It fuses gradually from 80° to 90°, gives off water, and the anhydrous residue fuses between 110° and 120°. It is formed in concentrated solutions, best when they contain more than the calculated amount of caesium thiocyanate, and when the excess of the latter is very large it crystallizes beside the double salt. By cooling a very concentrated solution of the salt it is possible to recrystallize it, but the 1 : 1 salt is deposited if the solution is more dilute.

The following analyses of different crops were made:

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[1] Pogg. Ann., **56**, 63.

	Calculated for $Cs_4Cd(SCN)_6.2H_2O$.	Found.			
		I.	II.	III.	IV.
Cs	51.73	....	....	....	....
Cd	10.93	10.66	....	....	....
SCN	33.84	33.59	33.65	33.67	33.88
H_2O	3.50	3.27	....	....	....

Anhydrous, 2 : 1 : 2, Caesium-Cadmium-Silver Thiocyanate, $Cs_2CdAg_2(SCN)_6$.—This salt is deposited on cooling and standing from solutions of almost any mixture of the three salts unless they are very dilute. When it forms rapidly it produces an exceedingly finely divided, snow-white precipitate. When it deposits more slowly it usually forms small, compact, spherical, white concretions in which the individual crystals are difficult to detect, even with a microscope of high power. In rather concentrated solutions, however, particularly those containing a very large excess of caesium thiocyanate, it is possible to obtain the compound in the form of groups of brilliant, thin scales, which are sometimes several millimeters in diameter. The best crystallized crops were obtained from a solution containing about 150 grams of caesium thiocyanate, 10 grams of cadmium thiocyanate, and 5 grams of silver thiocyanate at volumes varying from 250 to 300 cc. The readiness with which this compound is formed is a great obstacle to the preparation of the hydrous salt corresponding to it.

Analyses were made of several crops. No. I. was in the form of small spherical masses, No. II. was a precipitate, Nos. III., IV., and V. were in the form of small scales:

	Calculated for $Cs_2CdAg_2(SCN)_6$.	Found.				
		I.	II.	III.	IV.	V.
Cs	28.23	....	....	....	....	....
Cd	11.92	12.92	11.95	....	....	....
AgSCN	35.23	34.99	34.01	....	....	....
Sol. SCN	24.62	24.84	23.46	25.03	25.04	24.46

Hydrous, 2 : 1 : 2, Caesium-Cadmium-Silver Thiocyanate, $Cs_2CdAg_2(SCN)_6.2H_2O$.—This salt forms transparent, prismatic crystals. Usually the crystals form groups, radiating from common points, with the individuals a centimeter or more in length and about a millimeter in diameter, but sometimes loose masses are formed when the individual crystals are often exceedingly small and slender. The salt was observed under a wide range of conditions, but it does not appear to be formed readily in solutions containing a great excess of cadmium thiocyanate. It is extremely difficult to obtain pure crops of this compound, because the anhydrous salt is almost invariably deposited with it or upon it. It is probably best to use caesium and cadmium thiocyanates in nearly the required proportion with comparatively little of the silver salt. Then, at a certain degree of dilution, the salt will be deposited after cooling, and, on rare occasions, it may be obtained free from the white concretions of the anhydrous salt. The salt loses water very quickly on exposure to the air, becoming white and opaque.

Water was determined in a sample of the transparent crystals with the following result:

	Calculated for $Cs_2CdAg_2(SCN)_6.2H_2O$.	Found.
H_2O	3.68	4.22

Three samples, made under widely varying conditions, were analyzed after they had lost water by exposure or by drying at 100°, with the following results:

	Calculated for $Cs_2CdAg_2(SCN)_6$.	Found. I.	II.	III.
Cs	28.23	....	....	....
Cd	11.92	12.25	....	....
AgSCN	35.23	34.81	34.98	35.14
Sol. SCN	24.62	24.96	24.95	24.66

2 : 1 : 4, Caesium-Cadmium-Silver Thiocyanate, $Cs_2CdAg_4(SCN)_8.2H_2O$.—This salt is deposited from very dilute solutions which contain a moderate or large excess of caesium thiocyanate in comparison with the cadmium thiocyanate present, and also from very dilute solutions containing the two salts in nearly equal quantities. When the cadmium salt is considerably in excess the salt

$$Cs_4Cd_3Ag_{10}(SCN)_{20}.6H_2O$$

appears to be the invariable product under otherwise similar conditions. The salt is deposited either by cooling or upon long standing, sometimes only after many days, as a solution evaporates spontaneously. The solutions from which it forms are so dilute that they can hold but little silver thiocyanate in solution, and the crops obtained, even with 1000 or 1200 cc. of solution, are so small that it is difficult to obtain enough for satisfactory analyses. The compound has been observed in three different habits: (1) Minute needles, 2 or 3 mm. in length, mostly in groups of a few individuals radiating from points. Under the microscope these crystals were made out to be hexagonal prisms with pyramids. Professor Penfield has kindly confirmed this observation, and upon comparing these needles with crystals of the 4 : 3 : 10 salt, to be described next in order, he was unable to perceive any relationship between the two kinds of crystals (Analysis I.). (2) Small, thin, diamond-shaped crystals formed slowly (Analysis II.). The crystals of this crop resembled strongly those of the next salt to be described. Professor Penfield, who kindly compared the two kinds of crystals, found them to have similar optical properties, and he thought that they were identical. The analyses show much difference, however. (3) Still smaller and thinner scales, of undetermined shape, formed rapidly by cooling from two very different solutions (Analyses III. and IV.).

The analyses follow:

	Calculated for $Cs_2CdAg_4(SCN)_8.2H_2O$.	Found.			
		I.	II.	III.	IV.
Cs	20.30	....	20.10	....	....
Cd	8.58	8.93	8.65	8.35	8.76
AgSCN	50.67	51.07	50.56	50.43	50.84
Sol. SCN	17.70	17.89	....	17.73	17.80
H_2O	2.75	3.12	....	....	....

4 : 3 : 10, Caesium-Cadmium-Silver Thiocyanate, $Cs_4Cd_3Ag_{10}(SCN)_{20}.6H_2O$.—This occurs in brilliant, colorless, or faint-yellowish crystals, sometimes 2 or 3 mm. in diameter, but usually smaller. The crystals appear to be orthorhombic in form, and are almost invariably of diamond-shaped (rhombic) outline, resulting from prominent faces forming rather low, elongated pyramids. The salt is deposited from dilute solutions containing greater quantities of cadmium thiocyanate than of the caesium salt, which are nearly saturated with silver thiocyanate, best by evaporation at ordinary temperatures. The crystals often form at the surface of the liquid, but they form also at the bottom. From the less dilute solutions the compound is frequently deposited together with the white spherules of $Cs_2CdAg_2(SCN)_6$, but it is formed alone when such solutions are sufficiently diluted. Many crops were prepared and analyzed, on account of the complex composition indicated. These crops came from two solutions, one of which contained a much greater excess of cadmium thiocyanate than the other, and during the progress of the experiments this excess was still further increased. Both solutions were gradually diluted, and the analyses are given in the order in which they were made, so that the analyses with higher numbers generally represent products from more dilute solutions than the preceding ones. The dilutions were carried to a point where but little silver thiocyanate could be dissolved in the solutions at about 1200 cc. (a portion of the liquid being removed at each step), and the crops of triple salt became too small for satisfactory analyses.

The analyses, all of which represent separate products, are given in the table on the opposite page.

It is to be observed that the crops from the more dilute solutions show a slight tendency to approach the composition represented by the simpler formula, but since all the crops were formed in the presence of an excess of cadmium thiocyanate, a deficiency in cadmium would not be expected in them, and hence the more complex formula has been reluctantly adopted.

Methods of Analysis.—In analyzing the salts described in this article, a substance containing silver was treated with a liberal amount of water, usually at boiling, for some time, then the silver thiocyanate was collected on a Gooch filter, dried at somewhat above 100°, and weighed. Cadmium was sometimes precipitated as sulphide, which was also weighed in a Gooch crucible. This was always the case where caesium was to be determined by weighing the normal sulphate. Cadmium was determined in other cases by precipitation with

	Calculated for $Cs_4Cd_3Ag_{10}(SCN)_{20}.6H_2O$.	Found.										Calculated for $CsCdAg_3(SCN)_6.2H_2O$
		I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	
Cs	16.54	....	....	16.38	....	....	16.58	15.97	15.91	....	....	13.95
Cd	10.48	9.99	....	10.26	10.26	10.47	10.70	10.48	10.46	10.40	10.98	11.79
AgSCN	51.60	51.74	51.57	51.91	51.95	51.18	51.60	52.04	51.96	52.04	52.05	52.23
Sol. SCN	18.03	18.36	18.26	....	18.08	18.25	....	....	....	....	....	18.25
H_2O	3.35	....	3.31	3.28	3.38	3.23	3.40	....	....	....	....	3.78

sodium carbonate and weighing the oxide in a Gooch crucible. This method frequently gave some trouble, as the carbonate was finely divided and difficult to filter, but in these cases the operation was repeated until the filtrate was clear. The filtrate from the cadmium carbonate was frequently titrated for soluble SCN, but sometimes a separate sample was used for this purpose. Water was determined by loss upon heating to constant weight, usually at about 120°.

NEW HAVEN, CONN., April, 1903.

Contributions from the Sheffield Laboratory of Yale University.

CVII.—ON A DOUBLE SALT OF POTASSIUM AND BARIUM NITRATES.

BY WM. K. WALLBRIDGE.

The salt to be described, $2KNO_3.Ba(NO_3)_2$, is of considerable interest, because other double salts of alkali metals and barium are apparently entirely unknown, and because, while a few double nitrates are known, no evidence has been obtained previously that alkaline nitrates form crystallizable double nitrates with the nitrates of bivalent metals.[1] For these two reasons, therefore, the salt is a very unusual one, and one whose existence would not be expected from analogy.

When a hot, concentrated solution of 40 grams of potassium nitrate and 10 grams of barium nitrate was allowed to cool, large crystals of potassium nitrate formed, and afterwards a crop of small, opaque crystals was deposited upon them. These were carefully picked out and dried by pressing with filter-paper (Analysis I.). On evaporation of the mother-liquor a similar crop was deposited upon potassium nitrate crystals (Analysis II.). The double salt, free from crystals of potassium nitrate, was then obtained from a solution of 40 grams of potassium nitrate and 20 grams of barium nitrate (Analysis III.). From a solution of 20 grams each of the two nitrates a crop was obtained which contained a much larger amount of barium than the double salt. This was evidently a mixture of the double salt with barium nitrate, but it was the only crop analyzed which indicated a mixture. From the mother-liquor from this mixture a crop of the double salt was obtained (Analysis IV.). Another crop was prepared by slow evaporation, over sulphuric acid, of a solution containing 40 grams of potassium nitrate and 20 grams of the barium salt (Analysis V.).

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[1] See Wells, Beardsley, and Jamieson : This JOURNAL, 26, 275.

The results of the analyses are as follows :

	Calculated for $K_2Ba(NO_3)_4$.	Found.				
		I.	II.	III.	IV.	V.
K	16.87	17.07	....	16.52	....	....
Ba	29.64	29.69	29.21	29.22	30.45	30.49
NO_3	53.49	52.95	....	52.62	....	....
H_2O	....	....	....	1.89	....	....

In regard to the analyses, it may be mentioned that barium and potassium were weighed as sulphates while nitrogen was determined by the modified Kjeldahl-Gunning method.[1]

The crystals formed by cooling were in white, opaque masses of microscopic individuals, which showed tetrahedral habit, while the crystals obtained by slow evaporation were very much larger, usually from 1 to 3 mm. in diameter. The latter were also white and opaque and were invariably of tetrahedral form. The faces of these crystals were much striated and very rough and imperfect. Prof. S. L. Penfield has kindly inspected the crystals, and has found that they show strong optical properties, although they are too opaque to give any satisfactory results upon examination. Professor Penfield has also pointed out the general resemblance in habit of these crystals to certain crystals of barium nitrate mentioned by Groth.[2] The view that the crystals are impure barium nitrate must therefore be considered. This does not appear to be possible on account of the constant composition of several crops produced under considerably different conditions, and also on account of the close ratios derived from the analyses, which indicate the presence of 2 atoms of potassium to 1 of barium. It should be mentioned also that when crystallizations were made from solutions containing more barium nitrate than potassium nitrate, or when an attempt was made to recrystallize the double salt, barium nitrate was deposited in crystals of octahedral habit, which were more transparent and were different in appearance from the double salt.

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[1] Bulletin 46, Revised Edition, U. S. Dept. Agr., p. 17.

[2] Physikal. Krystallog., p. 498.

Attempts to prepare a double salt with caesium nitrate and barium nitrate were without success. From a solution containing 25 grams of the caesium salt and 15 grams of the barium salt, the two simple salts crystallized out side by side. A similar result was obtained with potassium nitrate and strontium nitrate, for it was found that these two salts crystallized side by side when 10 grams of the first and 18 grams of the second were present in a solution. It does not appear probable, therefore, that a series of double nitrates analogous to $K_2Ba(NO_3)_4$ can be prepared.

It may be said, in conclusion, that the double salt under consideration is curious, not only as an alkali-metal and barium double nitrate, but because a corresponding compound is not formed by caesium, which shows an eminent tendency to form double salts, and also because it crystallizes in imitation of barium nitrate and forms very crude, opaque crystals. It seems possible that these crystals are formed upon nuclei of barium nitrate and that their structure is pseudomorphic.

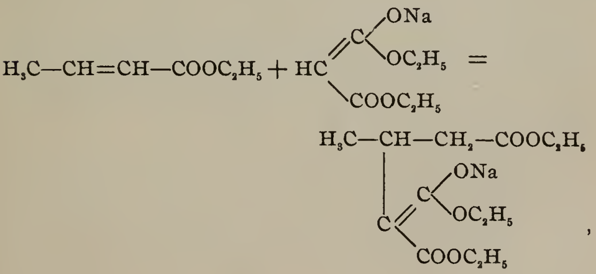
NEW HAVEN, CONN., April, 1903.

ON THE CONDENSATION OF OXALIC ETHYL ESTER WITH ETHYLENE AND TRIMETHYLENE CYANIDES.

BY ARTHUR MICHAEL.

According to v. Baeyer's strain hypothesis, the facility of the conversion of organic substances with open into those with closed chains is dependent on the spacial proximity of the groups that interact to form the ring. Basing his speculations on the van 't Hoff tetrahedron form for the carbon atom, v. Baeyer showed that the strain hypothesis explains the well-known tendency towards the formation of derivatives containing five- or six-membered rings. Although a very considerable number of facts are in accordance with these views, the strain hypothesis cannot represent a comprehensive explanation for the theory of ring-formation, since it does not take into consideration the question of chemical affinity, nor the influence of side-chains in facilitating such condensations.

That groups, which do not directly enter into the process of forming the ring, may greatly influence the phenomenon has long been known, but until recently the facile condensation of substances with open to those with closed chains invariably implied the formation of derivatives containing a five- or six-membered ring. Indeed, this relationship forms the principal support of the strain hypothesis. Several years ago the writer[1] showed that, through the indirect influence of certain side groups, derivatives of tetramethylene may be obtained not only by alcohol-condensation, but that they are quite as readily formed as any derivatives of five- or six-membered rings. Thus the substance formed by addition of sodium malonic ester to crotonic ester,



is stable, but if *β*-carbethoxycrotonic ester, *i. e.*, citraconic ester be used, instead of crotonic ester, a very considerable part of the addition-product formed at first undergoes a spontaneous condensation to a derivative of ketotetramethylene :

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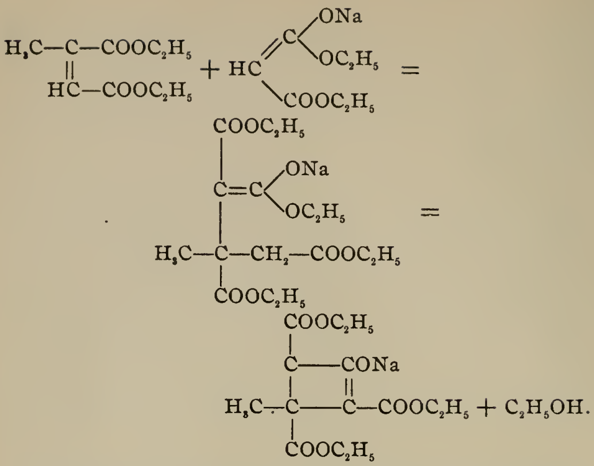
[1] Ber. d. chem. Ges., 33, 3742.



Furthermore, it was shown that methyl and, to a greater degree, ethyl facilitate these condensations more or less, according to their position towards the malonic-ester radical of the addition-products. This investigation proves conclusively that the strain hypothesis will require material modification before it can offer a satisfactory explanation of the phenomenon of ring-formation, but in this paper it is not proposed to enter more fully on the subject.

In continuing this investigation on the influence of side-chains, some experiments were made to ascertain whether derivatives of tetramethylene could be obtained by means of oxalic ester. The use of succinic ester as second substance for this purpose was debarred, since it readily suffers a chemical change with sodium or sodium ethylate, and succinic nitrile was therefore employed in its place.

The condensation of oxalic ester with benzyl nitrile has been effected by Erlenmeyer, Jr.[1] Subsequently, Fleishhauer[2] extended the reaction, using several fatty nitriles. In the later experiments only poor yields were obtained, but in syntheses like the above it is characteristic of the indirect influence of negative, polyvalent atoms in the fourth position towards the carbon of a methylene group, to greatly facilitate the reactivity of hydrogen joined to such carbon,[1] and since ethylene cyanide fulfils these conditions, more favorable results were expected than when monobasic nitriles are used. The condensation between oxalic ester and ethylene nitrile, using either sodium ethylate or sodium, proceeds readily and a fair yield of a keto-product is formed. The reaction, however, does not lead to a product with a closed chain, but proceeds as follows:

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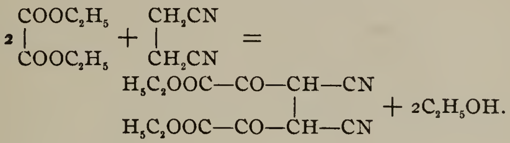
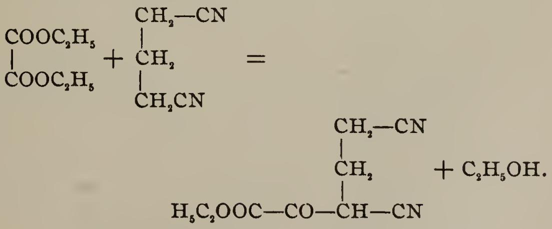
[1] Ber. d. chem. Ges., **22**, 1483.

[2] J. prakt. Chem., [2], **47**, 375.



$$2\begin{array}{l}\mathrm{COOC_2H_5}\\ |\\ \mathrm{COOC_2H_5}\end{array}+\begin{array}{l}\mathrm{CH_2CN}\\ |\\ \mathrm{CH_2CN}\end{array}=\begin{array}{r}\mathrm{H_5C_2OOC{-}CO{-}CH{-}CN}\\ |\qquad\quad\\ \mathrm{H_5C_2OOC{-}CO{-}CH{-}CN}\end{array}+2\mathrm{C_2H_5OH}.$$

Since Dieckmann[2] has shown that ketopentamethylene derivatives may be easily synthesized by condensing oxalic ester with glutaric ester, it was expected that using trimethylene cyanide, instead of the ethylene derivative, an analogous product would be obtained. It was found, however, that condensation stops at the first stage of the reaction and attempts to close the chain were without result. The reaction is represented by:



$$\begin{array}{l}\mathrm{COOC_2H_5}\\ |\\ \mathrm{COOC_2H_5}\end{array}+\begin{array}{l}\mathrm{CH_2{-}CN}\\ |\\ \mathrm{CH_2}\\ |\\ \mathrm{CH_2CN}\end{array}=\begin{array}{r}\mathrm{CH_2{-}CN}\\ |\qquad\quad\\ \mathrm{CH_2}\qquad\;\;\\ |\qquad\quad\\ \mathrm{H_5C_2OOC{-}CO{-}CH{-}CN}\end{array}+\mathrm{C_2H_5OH}.$$

Action of Oxalic Ester on Ethylene Cyanide.

Five grams of ethylene cyanide[2] were dissolved in 9 grams oxalic ethyl ester (equal mols.), the solution cooled to room temperature, and 1.4 grams sodium wire (1 atom) added. The reaction began soon, but was slow, and after the mixture had stood a day there was still a little unchanged sodium. It was finally completed by warming the mixture to about 45° for a short time. Only a small amount of gas was given off. The product, which was a canary-yellow substance suspended in a thick oil, was dissolved with cold water and filtered from a slight residue. Carbon dioxide, passed through the filtrate, gave no precipitate, but addition of hydrochloric acid gave a thick oil. On standing for a day in the ice-chest, this oil solidified to a considerable extent to long, yellowish prisms, which were filtered off under pressure and washed with a little dilute alcohol. For analysis, the dried product was taken up with hot benzene, filtered from a small amount of insoluble, resinous substance, and recrystallized twice from the same solvent.

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[1] Michael: Ber. d. chem. Ges., 33, 3733.

[2] Ann. Chem. (Liebig), 317, 27.

I. 0.1314 gram substance, dried at 100° *in vacuo*, gave 0.2473 gram CO_2 and 0.0556 gram H_2O.

II. 0.1533 gram substance, dried at 100° *in vacuo*, gave 0.2878 gram CO_2 and 0.0653 gram H_2O.

III. 0.3075 gram substance, dried at 100° *in vacuo*, gave 29 cc. N at 22° and 757 mm.

	Calculated for $C_{12}H_{12}O_6N_2$.	Found.		
		I.	II.	III.
C	51.4	51.3	51.2	...
H	4.3	4.7	4.7	...
N	10.0	...	...	10.6

β,γ-Dicyano-α,δ-diketoadipic ethyl ester crystallizes from alcohol as long, straw-colored prisms, with obliquely truncated ends, which often form fan-shaped groups. It melts under boiling water, but is only sparingly soluble in it. In alcohol it dissolves readily in the cold, also in hot benzene, separating from the latter solvent, on cooling, as small, prismatic needles, which melt at 121° to 123°. Hot petroleum ether dissolves the substance but slightly. Boiled with dilute hydrochloric acid, it is easily saponified, giving a thick oil, which was not further examined. The ester gives the hydrazone reaction with phenylhydrazine acetate. The substance may be obtained by using alcoholic sodium ethylate instead of sodium. To a cold solution of 1.6 grams sodium (2 atoms) in 20 grams absolute alcohol, 10.8 grams oxalic ester and 3 grams ethylene cyanide (1 mol.) were added. A precipitate began to form in a short time, which increased on allowing the mixture to stand. After addition of some absolute alcohol to this product it was filtered under pressure, washed with alcohol, and dried on a porous plate. This substance forms canary-yellow prisms that are insoluble in hot benzene, acetic ester, and chloroform, and melt at 92° to 96°. In warm absolute alcohol it dissolved readily, but it underwent a change, as the precipitate deposited from the solution on cooling was now not soluble in warm alcohol. The yellow substance contained sodium, and the addition of a mineral acid to its solution in cold water gave a precipitate which, after recrystallization from benzene, melted at 121° to 123° and was identical with the condensation-product obtained by using sodium. It was apparently the sodium derivative of the dicyanoketoadipic ester.

Action of Oxalic Ethyl Ester on Trimethylene Cyanide.

In preparing trimethylene cyanide, according to the directions given by Henry,[1] a potassium cyanide was employed that was supposed to be a 98 to 99 per cent pure product. On fractionating the product of the reaction, some oil was obtained that boiled considerably lower than trimethylene cyanide, and after several fractionations with beads in vacuum, 5 grams (from 137 grams trimethylene bromide) of an oil, boiling constantly at 91° C. under 12 mm. pressure, were isolated. The product contained bromine and, as the following halogen estimation showed, was formed by the replacement of one bromine in trimethylene bromine by the cyanogen radical:

0.2052 gram oil gave 0.2597 gram AgBr.

	Calculated for $CH_2Br—CH_2—CH_2—CN$.	Found.
Br	54.2	53.8

The formation of this substance is analogous to that of trimethylene chlorocyanide from trimethylene chlorobromide and potassium cyanide. Its appearance was probably due to the use of potassium cyanide, which was less pure than was supposed, since a subsequent preparation of the cyanide, when pure potassium cyanide was employed, gave only trimethylene cyanide.

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[1] Compt. rend., **100**, 742.

To a solution of 5 grams trimethylene cyanide in 7.8 grams oxalic ethyl ester (equal mols.) 1.25 grams sodium wire (1 atom) were added and, as the metal did not react in the cold, the mixture was heated to 40°, when the reaction began. The flask was then removed from the water-bath and in about an hour, at room temperature, almost all the metal was used up. The few remaining shreds of sodium disappeared on warming the flask gently for an hour. The brown product was taken up with cold water and carbon dioxide passed through the solution as long as a precipitate was formed. This precipitate was inconsiderable and was not examined. The addition of hydrochloric acid to the filtrate from this precipitate gave an oil that soon solidified to a mass (4 grams) of large crystals. For analysis the substance was treated in benzene solution with bone-black, and recrystallized twice from that solvent and then once from hot water.

0.1359 gram substance gave 0.2773 gram CO_2 and 0.0678 gram H_2O.

0.3700 gram substance gave 49 cc. N at 21° and 754.6 mm.

	Calculated for $C_9H_{10}O_3N_2$.	Found.
C	55.7	55.6
H	5.1	5.5
N	14.4	14.8

β,δ-Dicyano-α-ketoglutaric ester crystallizes from benzene as almost white, six-sided prisms, generally with truncated ends, that melt at 96° to 98°. It is but slightly soluble in cold water and benzene; readily in these solvents when hot; and sparingly soluble in ligroin, ether, and carbon tetrachloride. In dilute alkalies it dissolves and is precipitated unchanged by addition of a mineral acid to the solution. The ester gives with phenylhydrazine acetate the hydrazone reaction for the presence of a keto group. Boiled with dilute hydrochloric acid it was easily saponified, with evolution of carbon dioxide, and a thick, oily acid was formed, which could not be obtained in a solid state.

The substance was also prepared by using alcoholic sodium ethylate. One gram sodium (1 atom) was dissolved in 12 grams absolute alcohol, the solution cooled, 6 grams oxalic ester (1 mol.) and then 4 grams trimethylene cyanide (1 mol.) added. The mixture was placed a day in the ice-chest and then allowed to stand for several days at the temperature of the room. A crystalline precipitate formed, which was filtered, washed with alcohol, and then dissolved in water. Addition of hydrochloric acid to the aqueous solution gave 3.9 grams of the substance in an almost pure state.

Several experiments were made to obtain a cyclopentene derivative from oxalic ester and trimethylene cyanide. The experiment just described was repeated with the variation of using 2 molecules of sodium ethylate to 1 molecule of cyanide. The solution became dark-red after standing several days, but no precipitate was formed. After evaporation of the alcohol in vacuum, the residue was dissolved in water and a slight excess of hydrochloric acid added to the solution. The copious precipitate was not a pure substance, it melting partially at 78° to 80° and at 175° to 185°, and left a mineral residue on calcination. Extracted with hot benzene, about two-thirds dissolved, and the above-described keto ester separated from the solution on cooling. Equally unsuccessful was an experiment using 2 atoms sodium to 1 molecule of the cyanide, and also the action of sodium ethylate on the dicyanoketoglutaric ester.

A number of experiments were made to obtain condensation-products of ethylene and trimethylene cyanides with mono- and diethyl malonic and glutaric esters, using sodium for the purpose. The metal did not act readily on these mixtures and heat was required to use it up. In no case was more than a small yield of an acidic oil obtained.

TUFTS COLLEGE, MASS.

REVIEWS.

The Story of Alchemy and Beginners of Chemistry. By M. M. Pattison-Muir. New York: D. Appleton & Co. 1903. pp. 185.

In the last fifteen years Berthelot has minutely described in six folio volumes the beginning of alchemy in Egypt and shows how the art, surviving the destruction of the Alexandrian library and the Roman eviction of the alchemists from Egypt, wandered degraded through Chaldea and Mesopotamia to Constantinople and how finally, reaching Europe in the thirteenth century, misunderstood even by its promoters, it took the same disgraceful rank as astrology and magic.

It is surprising, at this late day, to find Mr. Muir describing the alchemy of the sixteenth century as alchemy *par excellence*, and so condemning it as unintelligible and comparing the tottering structure with the philosophical systems of the Greeks. Two facts need to be held in mind to give us a clear view of this subject. First, alchemy was an art—it was neither a philosophical or theological system; second, it was, as an art or handicraft, Egyptian, and its literature and language, even in the sixteenth century, may be made surprisingly intelligible by reflecting upon it the Egyptian conception of nature.

The later alchemy may contain "A language that is inexact, undescriptive, and unsuggestive to modern ears," and yet we are not justified in speaking, as does Mr. Muir on his opening page, of "One very curious manufacture wherein not the thousandth fragment of a grain of the finished article was ever produced." No portion of what we now understand as gold was ever produced, yet, what the Egyptian meant by gold was produced abundantly, for, in Egypt, "gold" meant often a purple bronze or iridescence. (*Chemical News*, **85**, 49.)

The author's general attitude towards alchemy, as he interprets it, is condemnatory. So far as page 122 he describes the bombast and fairy tales of the period as though they were essential parts of a system. Chapter VI., however, contains a very good description of "Alchemy as an experimental art," fully illustrated by cuts. The errors of the work may perhaps be answered curiously enough by Mr. Muir's own words: "It would be truly absurd to carry back to that time the meaning that we give to these terms to-day and then to brand as ridiculous the attempts of the men who studied then the same problems that we study now."

The last third of the book is devoted to a masterly description of the transition from alchemy to the chemistry of Lavoisier. Here the author is strong and the theme is well sustained to the end. The book is small, with flexible covers. It is published in an attractive form as one of "The Library of Useful Stories," and, taken as a whole, is a delightful book to read. A. J. H.

MONOGRAPHIEN ÜBER ANGEWANDTE ELEKTROCHEMIE. II. BAND. DIE GEWINNUNG DES ALUMINIUMS, UND DESSEN BEDEUTUNG FÜR HANDEL UND INDUSTRIE. Von ADOLPHE MINET. Ins Deutsche übertragen von DR. EMIL ABEL. Wien: Wilhelm Knapp. Halle, a. S. 1902.

As the title implies, the monograph discusses the various methods by which the element aluminium is obtained. The methods are divided into two general classes—chemical and electrochemical. The former include the reduction of aluminium compounds by sodium and other substances, and the latter the various electrical processes which have been employed in obtaining aluminium.

The work in hand contains a discussion of much of the same material included by Borchers in his "Elektrometallurgie." The second part of this monograph takes up such questions as the cost of producing aluminium, the alloys of aluminium, and the aluminium industry in general. H. C. J.

MONOGRAPHIEN ÜBER ANGEWANDTE ELEKTROCHEMIE. III. BAND. DIE DARSTELLUNG DES CHROMS UND SEINER VERBINDUNGEN, MIT HILFE DES ELEKTRISCHEN STROMES. Von DR. MAX LA BLANCORD, Professor und Direktor des Physikalisch-chemischen (Elektrochemischen) Instituts der Technischen Hochschule zu Karlsruhe. Halle, a. S. Wilhelm Knapp. 1902.

This monograph on the preparation of chromium and its compounds gives a review of the electrical methods used for that purpose up to the end of the year 1901. The methods are classified under the general heads: Preparation of metallic chromium by electrolysis from aqueous solution, and at high temperatures; preparation of compounds of chromium with metals by electrolysis from aqueous solution, and at high temperatures; and preparation of the compounds of chromium with the non-metals, such as carbon, silicon, phosphorus, sulphur, oxygen, etc.

The work is written with that unusual clearness which is characteristic of its author. H. C. J.

PHYSICAL CHEMISTRY FOR PHYSICIANS AND BIOLOGISTS. By DR. ERNST COHEN, Professor of General and Inorganic Chemistry in the University of Utrecht. Authorized translation from the German, by MARTIN H. FISCHER, M.D., Instructor in Physiology in the University of California. New York: Henry Holt & Co. 1903. pp. 343.

The work in hand was prepared, according to the author, "in response to the request of a number of physicians to give in a series of lectures a résumé of those subjects in physical or general chemistry which are of importance in medicine. These lectures are in no way a text-book of physical chemistry. I have merely endeavored to show in them the close relation that exists between this new branch of chemistry and the biological sciences." The lectures are on reaction velocity, inversion of cane-sugar and catalysis in general, the action of ferments, temperature and reaction velocity, equilibrium, friction of liquids, osmotic pressure, molecular weight of dissolved substances, the theory of electrolytic dissociation, applications. The importance of physical chemistry in connection with the biological sciences is becoming greater and greater, and there is a growing demand on the part of biologists to know more and more of the recent developments in physical chemistry. The book under consideration will undoubtedly prove useful in the field which it is meant to cover. A question which may fairly be raised is whether the average physician is sufficiently familiar with the calculus and differential equations to use successfully a work into which they are extensively introduced. The work is clearly written, and the English translation seems to be satisfactory. H. C. J.

INORGANIC CHEMISTRY SYLLABUS. By HUBERT C. CAREL, B.S., Assistant Professor in the University of Minnesota. Third Edition. Minneapolis: H. W. Wilson. 1902.

The author's preface says that "this little book is an effort to present in brief form, those salient facts of inorganic chemistry as offered to the Freshman classes of the Department of Medicine, University of Minnesota. The chief object has been brevity, to which we have sacrificed everything save accuracy and definition." The writer has been successful, for the book contains a surprising amount of condensed descriptive chemistry. Indeed, there is almost too much detail for a book in which the single subjects are treated so briefly, and there would be danger of the student not grasping the relative value of the facts presented, were the book used alone, but used as it is with lectures and laboratory, it is doubtless of value. E. R.

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AMERICAN

CHEMICAL JOURNAL

Contributions from the Sheffield Laboratory of Yale University.

CVIII.—ON SOME PSEUDODITHIOBIURETS.

BY TREAT BALDWIN JOHNSON.

The non-substituted pseudothioureas,

$$NH{=}C(SR){-}NH_2(R{=}CH_3{-},C_2H_5{-}),$$

have received very little attention. It is only recently that they have been found to be capable of isolation. In some previous papers from this laboratory[1] it has been shown that the free pseudothioureas are not so unstable as one would be led to believe, and it has been found that they can be isolated from their halide salts at low temperatures.

The work described in this paper was undertaken at the suggestion of Prof. H. L. Wheeler, with the object of investigating the action of isothiocyanates on these simple pseudothioureas, and also some of the type

$$RN{=}C(SR'){-}NH_2(R{=}C_6H_5,C_7H_7{-}).$$

I find that the non-substituted pseudothioureas are fairly stable in aqueous solution at ordinary temperature, and combine very smoothly with isothiocyanates, giving a new class of pseudodithiobiurets.

The first pseudodithiobiurets were prepared by Tursini[2] by treating phenyldithiobiuret and paratolyldithiobiuret with ethyl iodide in the presence of ammonia. He also mentions the corresponding pseudomethyl derivatives. Tursini showed that the alkyl radical was joined to sulphur, but did not determine to which sulphur atom it had attached itself.

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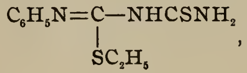
[1] This JOURNAL, **29**, 478, 492 (1903).

[2] Ber. d. chem. Ges., **17**, 585.

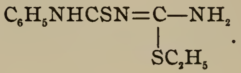
Billeter[1] has described a somewhat different type of pseudodithiobiurets, which he obtained by treating certain thioureas with thiocarbamic chlorides. He furthermore made the interesting observation that his pseudodithiobiurets underwent a molecular rearrangement into the normal dithiobiurets.

There are two structurally different pseudodithiobiurets, since tautomeric forms need not be considered, having the composition of Tursini's phenyl derivative:



$$C_6H_5N{=}\underset{\substack{|\\ SC_2H_5}}{C}{-}NHCSNH_2,$$

I.

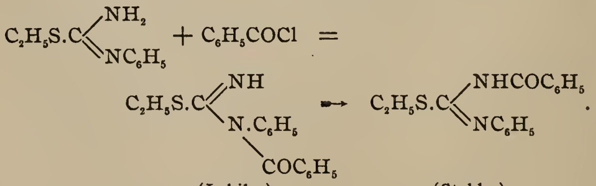


$$C_6H_5NHCSN{=}\underset{\substack{|\\ SC_2H_5}}{C}{-}NH_2.$$

II.

We have prepared the pseudoethyldithiobiuret (Formula II.) by treating pseudoethylthiourea with phenyl isothiocyanate. We find that it does not agree in any of its properties with Tursini's body. Tursini's pseudoethyldithiobiuret must, therefore, be the isomeric substance having the structure shown in Formula I.

In a previous paper[2] from this laboratory it has been shown that when a substituted pseudothiourea is treated in the cold with an acid chloride that the acyl radical first attacks the nitrogen atom which is joined to the aryl group. An unstable acyl derivative is formed, which very easily undergoes a molecular rearrangement into a stable isomer.



(Labile.) (Stable.)

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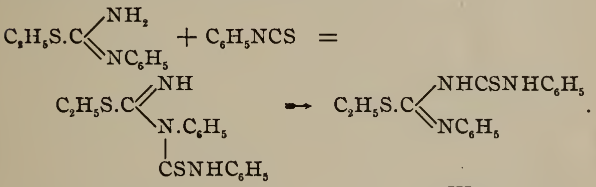
[1] *Ibid.*, **21**, 108; **26**, 1688.

[2] This JOURNAL, **27**, 270 (1902).

Busch and Holzmann[1] made a similar observation in the action of isothiocyanates on phenylhydrazine. Contrary to the rule of stereochemical interference, it was the nitrogen atom attached to the phenyl group which was the first point of attack by the isothiocyanate. Labile products were obtained which underwent a metastatic change into symmetrical thiosemicarbazides.

It might be expected, like the above, that when an isothiocyanate is allowed to act on a substituted pseudothiourea an analogous reaction would take place; that a labile product would first be formed, which would undergo a molecular rearrangement into a stable isomer:



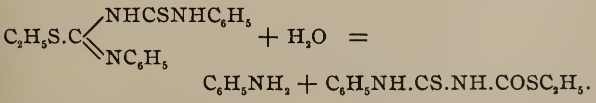
$$C_2H_5S.C\left\langle\begin{matrix}NH_2\\ NC_6H_5\end{matrix}\right. + C_6H_5NCS =$$

$$C_2H_5S.C\left\langle\begin{matrix}NH\\ N.C_6H_5\\ |\\ CSNHC_6H_5\end{matrix}\right. \longrightarrow C_2H_5S.C\left\langle\begin{matrix}NHCSNHC_6H_5\\ NC_6H_5\end{matrix}\right. .$$

III.

(Labile.) (Stable.)

We find that isothiocyanates react with the aromatic substituted pseudothioureas with extreme smoothness. They react best at ordinary temperatures and yield quantitatively pseudodithiobiurets. With the various pseudothioureas, which we have examined, we have not observed the formation of any labile products. The isothiocyanate unites with the amino radical of the pseudothiourea in preference to the nitrogen which is attached to the aryl group. The structure of the pseudodithiobiurets is shown in Formula III., since on hydrolysis they decompose as represented in the following equation:



$$C_2H_5S.C\left\langle\begin{matrix}NHCSNHC_6H_5\\ NC_6H_5\end{matrix}\right. + H_2O =$$

$$C_6H_5NH_2 + C_6H_5NH.CS.NH.COSC_2H_5.$$

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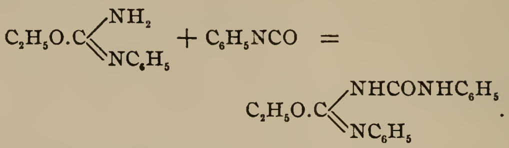
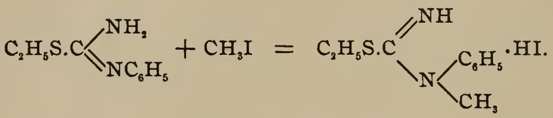
[1] Ber. d. chem. Ges., 34, 320 (1901).

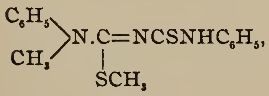
Our results are perfectly analogous to those of McKee,[1] who described the behavior of phenyl isocyanate towards the oxygen pseudoureas :



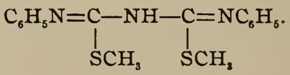
Bertram[2] has shown that when phenylthiolmethylpseudothiourea is treated with a molecular proportion of methyl iodide, that the methyl radical attaches itself to the nitrogen atom which is joined to phenyl :



Theoretically, an analogous addition might be expected to take place by treating our pseudodithiobiurets with methyl iodide (Formula IV.), or the methyl radical would attach itself to sulphur, giving a dipseudodithiobiuret (Formula V.).



IV.



$$C_6H_5N{=}\underset{SCH_3}{\underset{|}{C}}{-}NH{-}\underset{SCH_3}{\underset{|}{C}}{=}NC_6H_5.$$

V.

We find that our pseudodithiobiurets add on methyl iodide very smoothly, giving products which are well crystallized and easy of purification. That the alkyl radicals in these addition-bodies are attached to sulphur and not to nitrogen is proved by the following experiments :

I. When *a*-phenyl-*a*-methylthiolmethylpseudothiourea is treated with phenyl isothiocyanate a different biuret is obtained than when methyl iodide is added to *a*,*c*-diphenyl-1-thiolmethylpseudodithiobiuret:[1]

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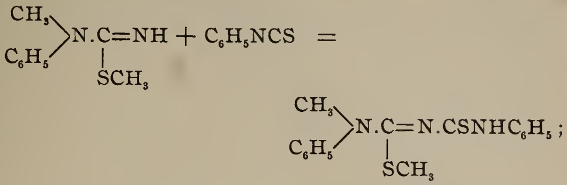
[1] This Journal, **26**, 209 (1901).

[2] Ber. d. chem. Ges., **25**, 52.

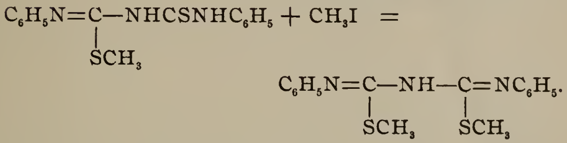
a.



VI.

(*a*,*c*-Diphenyl-*a*-methyl-1-thiol-methylpseudodithiobiuret.)

b.

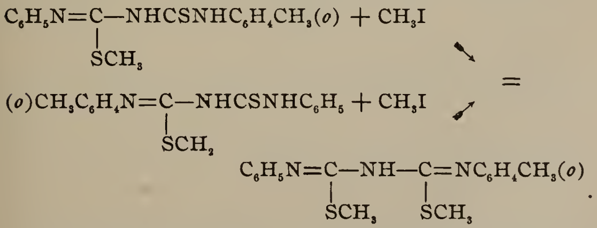


$$C_6H_5N{=}\underset{\substack{|\\ SCH_3}}{C}{-}NHCSNHC_6H_5 + CH_3I = C_6H_5N{=}\underset{\substack{|\\ SCH_3}}{C}{-}NH{-}\underset{\substack{|\\ SCH_3}}{C}{=}NC_6H_5.$$

VII.

(*a*,*c*-Diphenyl-1,2-thiolmethyldi-pseudodithiobiuret.)

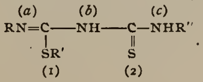
II. The same dipseudodithiobiuret results when *a*-phenyl-*c*-orthotolyl-1-thiolmethylpseudodithiobiuret is treated with methyl iodide, as is obtained by the action of methyl iodide on *a*-orthotolyl-*c*-phenyl-1-thiolmethylpseudodithiobiuret:



$$\left.\begin{array}{l} C_6H_5N{=}\underset{\substack{|\\ SCH_3}}{C}{-}NHCSNHC_6H_4CH_3(o) + CH_3I \searrow \\ (o)CH_3C_6H_4N{=}\underset{\substack{|\\ SCH_2}}{C}{-}NHCSNHC_6H_5 + CH_3I \nearrow \end{array}\right. = C_6H_5N{=}\underset{\substack{|\\ SCH_3}}{C}{-}NH{-}\underset{\substack{|\\ SCH_3}}{C}{=}NC_6H_4CH_3(o).$$

---

[1] In the dithiobiurets the nitrogen atoms will be designated alphabetically—*a*, *b*, *c*—; The sulphur atoms will be designated numerically—1, 2—:



$$\overset{(a)}{RN}{=}\underset{\substack{|\\ SR'\\ (1)}}{C}{-}\overset{(b)}{NH}{-}\underset{\substack{\|\\ S\\ (2)}}{C}{-}\overset{(c)}{NHR''}.$$

It has been shown in previous papers from this laboratory[1] that when two of the radicals—S.alk—, O.alk—, CO—, CS— are present in certain compounds, that they react with the amino hydrogen of phenylhydrazine in the following order:

$$—S.R > —CS > —CO > —OR.$$

Our pseudodithiobiuret seemed suitable for making a further test of this law, since both a mercapto and a thion grouping are present. We found, however, that our dithiobiurets reacted abnormally with phenylhydrazine. Instead of reacting to give triazole derivatives the phenylhydrazine simply removed the mustard oil from the pseudodithiobiuret, forming diphenylthiosemicarbazide.

EXPERIMENTAL PART.

BY HOWARD S. BRISTOL.

a-Phenyl-1-thiolmethylpseudodithiobiuret, $C_6H_5N{=}C(SCH_3)NHCSNH_2$.—This pseudodithiobiuret has previously been mentioned by Tursini,[2] but he did not describe its properties or give the melting-point of the body. We prepared it according to Tursini's directions by treating phenyldithiobiuret with methyl iodide in the presence of ammonia. It crystallized from alcohol in long prisms and melted at 122°. A nitrogen determination gave:

	Calculated for $C_9H_{11}N_3S_2$.	Found.
N	18.66	18.20

a-Phenyl-2-thiolmethylpseudodithiobiuret, $C_6H_5NHCSNHC(SCH_3){=}NH$. — This pseudodithiobiuret was obtained by allowing phenyl isothiocyanate to act at ordinary temperature on thiolmethylpseudothiourea. The methyl iodide addition-product of thiourea was dissolved in the least possible quantity of water and the free pseudothiourea precipitated with one molecular proportion of potassium hydroxide. To this aqueous solution of the free base was added a molecular proportion of phenyl isothiocyanate. The mixture was then allowed to stand, with occasional shaking, for twelve hours at ordinary laboratory temperature. A white solid separated in the form of balls, which was purified by crystallizing from alcohol. It separated in the form of prisms and melted with effervesence at 124°. When it was mixed with the above pseudodithiobiuret of Tursini's, melting at 122°, the melting-point was lowered to 102°. A nitrogen determination gave:

---

[1] This JOURNAL, **27**, 258 (1902); **29**, 73 (1903).

[2] *Loc. cit.*

	Calculated for $C_9H_{11}N_3S_2$.	Found.	
		I.	II.
N	18.66	18.53	18.56

When this pseudothiobiuret was boiled in alcoholic solution with phenylhydrazine, phenyl isothiocyanate was split off, yielding diphenylthiosemicarbazide melting at 176°. When mixed with pure diphenylthiosemicarbazide the melting-point was not changed.

a-Phenyl-2-thiolethylpseudodithiobiuret, $C_6H_5NHCSNHC(SC_2H_5){=}NH$.—This dithiobiuret was obtained by allowing phenyl isothiocyanate to combine with thiolethylpseudothiourea. The method of procedure was the same as in the preceding preparation of the methyl derivatives. A yellow solid was obtained which separated from dilute alcohol in the form of tables and melted at 114°. The yield was quantitative. A nitrogen determination gave:

	Calculated for $C_{10}H_{13}N_3S_2$.	Found.
N	17.57	17.46

Paratolylthiolmethylpseudothiourea, $(p)CH_3C_6H_4N{=}C(SCH_3)NH_2$.—This pseudothiourea has recently been described as an oil by Dixon,[1] who obtained it by the action of methyl chlorformate on paratolylthiourea. We have obtained the same pseudothiourea in the form of its hydriodide by warming on the steam-bath paratolylthiourea (moistened with alcohol) with a slight excess of methyl iodide. The hydriodide was obtained in the form of microscopic prisms, and after crystallization from a mixture of alcohol and ether it melted with effervescence at 129° to 130°. The free base was obtained by neutralizing an alcoholic solution of the hydriodide with sodium carbonate. It was exceedingly soluble in alcohol and was reprecipitated by water as an oil which solidified on long standing. It crystallized from petroleum ether in plates and melted at 65° to 67°. A nitrogen determination in the free pseudothiourea gave :

---

[1] J. Chem. Soc. (London), 83, 556 (1903).

	Calculated for $C_9H_{12}N_2S$.	Found.
N	15.50	15.60

The hydriodide was analyzed with the following result :

	Calculated for $C_9H_{13}N_2SI$.	Found.	
		I.	II.
N	9.09	9.41	9.25

a-Paratolyl-c-phenyl-1-thiolmethylpseudodithiobiuret, $(p)CH_3C_6H_4N{=}C(SCH_3)NHCSNHC_6H_5$. — This was obtained by allowing phenyl isothiocyanate to act for several hours at ordinary temperature on paratolylthiolmethylpseudothiourea, which had previously been dissolved in ether. By spontaneous evaporation of the ether, a crystalline body was obtained, which crystallized from alcohol in prisms and melted at 93°. It was very soluble in ether and warm alcohol, but insoluble in benzene and petroleum ether. A nitrogen determination gave :

	Calculated for $C_{16}H_{17}N_3S_2$.	Found.	
		I.	II.
N	13.33	13.18	13.20

When this dithiobiuret was boiled in alcoholic solution with a molecular proportion of phenylhydrazine, a slow reaction took place with formation of diphenylthiosemicarbazide. It melted at 174° to 175° with effervescence, and a nitrogen determination gave :

	Calculated for $C_{13}H_{13}N_3S$.	Found.
N	17.29	17.60

a-Paratolyl-c-phenyl-1,2-thiolmethyldipseudodithiobiuret, $(p)CH_3C_6H_4N = C(SCH_3)NHC(SCH_3) = NC_6H_5$. —— When *a*-paratolyl–*c*–phenyl–1-thiolmethylpseudodithiobiuret was treated in alcohol with a molecular proportion of methyl iodide a slow reaction took place with evolution of heat. After standing a few hours, beautiful, colorless prisms separated which melted, after several crystallizations from alcohol, at 164° with effervescence. A nitrogen determination agreed with the calculated for a methyl iodide addition-product. This hydriodide was rather difficultly soluble in water, but very soluble in warm alcohol. The free base was obtained by treating an alcoholic solution of the hydriodide with aqueous ammonia. It was precipitated as an oil, which showed no signs of solidifying after standing in an open dish for six weeks. A nitrogen determination in the hydriodide gave :

	Calculated for $C_{17}H_{19}N_3S_2.HI$.	Found.
N	9.19	9.39

a-Paratolyl-a-methylthiolmethylpseudothiourea, $(CH_3)(C_7H_7)N.C(SCH_3)=NH$.—This pseudourea was obtained in the form of its hydriodide by allowing methyl iodide to act on paratolylthiolmethylpseudothiourea. The reaction takes place with such violence that it is necessary to use a condenser. The methyl iodide addition-product was purified by crystallizing from a mixture of alcohol and ether, and it melted at 190° to 191° with effervescence. The free base was obtained as an oil by neutralizing an aqueous solution of the hydriodide with sodium carbonate. It showed no signs of crystallizing after standing for two months. The free base was thoroughly washed with water and dried over sulphuric acid. A nitrogen determination gave :

	Calculated for $C_{10}H_{14}N_2S$.	Found.
N	14.43	14.78

A nitrogen determination in the hydriodide gave :

	Calculated for $C_{10}H_{14}N_2S.HI$.	Found.
N	8.69	9.03

a-Paratolyl-a-methyl-c-phenyl-1-thiolmethylpseudodithiobiuret, $(CH_3)(C_7H_7)N.C(SCH_3)=NCSNHC_6H_5$.—This dithiobiuret resulted by allowing phenyl isothiocyanate to combine with *a*-paratolyl-*a*-methylthiolmethylpseudothiourea at ordinary temperature. The reaction was so energetic that much heat was evolved. It crystallized from alcohol in elongated prisms and melted at 124°. A nitrogen determination by the Kjeldahl method gave:

	Calculated for $C_{17}H_{19}N_3S_2$.	Found.
N	12.76	12.66

The hydriodide of this base was prepared by saturating a dry benzene solution of the base with hydriodic acid. It separated in the form of minute prisms and melted very sharply with effervescence at 182°. When this salt was mixed with its isomer—the hydriodide of *a*-paratolyl-*c*-phenyl-1,2-thiolmethyldipseudodithiobiuret—the mixture gave no definite melting-point, but melted all the way from 162° to 180°. A nitrogen determination gave:

	Calculated for $C_{17}H_{19}N_3S_2.HI$.	Found.
N	9.19	9.25

BY MORGAN S. ELMER.

a,c-Diphenyl-1-thiolmethylpseudodithiobiuret, $C_6H_5N{=}C(SCH_3)NHCSNHC_6H_5$.—This was obtained by allowing phenyl isothiocyanate to act on phenylthiolmethylpseudothiourea in ether solution at ordinary temperature. By spontaneous evaporation of the ether a crystalline body was obtained, which crystallized from alcohol in transparent, dog-tooth prisms and melted at 101°. A nitrogen determination gave:

	Calculated for $C_{15}H_{15}N_3S_2$.	Found.
N	13.95	14.45

Thiolmethyl Ester of Phenylthioallophanic Acid, $C_6H_5NHCSNHCOSCH_3$.—This ester was obtained by warming on the steam-bath *a,c*-diphenyl-1-thiolmethylpseudodithiobiuret with 50 per cent hydrochloric acid until complete solution was effected. Mercaptan was slowly evolved during the digestion. Upon cooling the acid solution, a mixture of plates and prisms separated. After several crystallizations from toluene, and then from chloroform, a body was obtained which melted sharply at 157° to 158° with effervescence. It crystallized from chloroform in plates and a nitrogen determination gave :

	Calculated for $C_9H_{10}ON_2S_2$.	Found.
N	12.40	12.68

a,c-Diphenyl-1,2-thiolmethyldipseudodithiobiuret, $C_6H_5N{=}C(SCH_3)NHC(SCH_3){=}NC_6H_5$.—This base was obtained in the form of its hydriodide by allowing methyl iodide to combine with *a,c*-diphenyl-1-thiolmethylpseudodithiobiuret. The salt crystallized from alcohol in stout prisms and melted with effervescence at 154° to 155°. An iodine determination gave :

	Calculated for $C_{16}H_{18}N_3S_2I$.	Found.
I	2.86	2.73

By treating an alcoholic solution of this hydriodide with a solution of sodium carbonate the free base was immediately precipitated in the form of colorless, needle-like prisms. It was recrystallized from alcohol and melted at 103° to 104°. A nitrogen determination gave :

	Calculated for $C_{16}H_{17}N_3S_2$.	Found.
N	13.33	13.56

a,c-Diphenyl-a-methyl-1-thiolmethylpseudodithiobiuret, $(CH_3)(C_6H_5)N{-}C(SCH_3){=}NCSNHC_6H_5$. — This pseudodithiobiuret resulted when phenyl isothiocyanate was allowed to combine with *a*-phenyl-*a*-methylthiolmethylpseudothiourea in ethereal solution. A colorless solid was formed which crystallized from alcohol in stout prisms and melted at 133° to 134°. A nitrogen determination gave :

	Calculated for $C_{16}H_{17}N_3S_2$.	Found.
N	13.33	13.38

a,c-Diphenyl-1-thiolbenzylpseudodithiobiuret, $C_6H_5N{=}C(SCH_2C_6H_5)NHCSNHC_6H_5$.—This pseudodithiobiuret was obtained by the action of phenyl isothiocyanate on phenylthiolbenzylpseudothiourea. The reaction-product was an oil, which finally solidified after standing about twenty-four hours. It crystallized from alcohol in colorless prisms and melted at 98° to 100°. It was soluble in benzene and insoluble in water. A nitrogen determination gave :

	Calculated for $C_{21}H_{19}N_3S_2$.	Found.
N	11.14	11.22

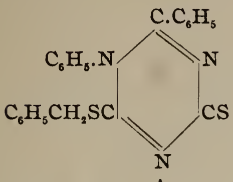
Phenylthiolbenzylpseudothiourea and Benzoyl Isothiocyanate.—Among the isothiocyanates which we used in our investigations was included benzoyl isothiocyanate. While the plain aryl isothiocyanates reacted with pseudothioureas generally very slowly with formation of colorless derivatives—dithiobiurets—benzoyl isothiocyanate reacted with such violence that it was necessary to dilute largely with benzene or ether in order to obtain a smooth reaction. It gave strong yellow- or orange-colored derivatives, which were more insoluble in the ordinary solvents than the dithiobiurets, and were insoluble in alkali.

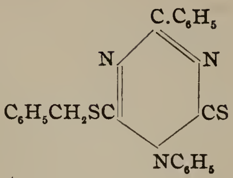
When phenylthiolbenzylpseudothiourea was dissolved in benzene and treated with benzoyl isothiocyanate, so much heat was evolved that it was necessary to connect with a condenser in order to prevent evaporation of the benzene. An oil separated from the benzene which finally solidified to a beautiful, yellow body. It crystallized from benzene in beautiful, yellow, stocky prisms and melted at 190° to 191°. It was insoluble in warm alcohol and water. Nitrogen and sulphur determinations indicated that we were not dealing here with a plain addition-product :

$$C_6H_5N{=}C(SCH_2C_6H_5)NHCSNHCOC_6H_5.$$

	Calculated for		Found.	
	$C_{22}H_{19}ON_3S_2$.	($C_{22}H_{17}N_3S_2$.)	I.	II.
N	10.37	10.85	10.88	11.07
S	15.80	16.54	17.24	....

The analytical determinations agreed favorably with the calculated for a triazine derivative. This could result by the loss of a molecule of water from the addition-product of the isothiocyanate and pseudothiourea. Two isomeric triazines are theoretically possible, depending on the point of attack of the isothiocyanate in the pseudourea. Which one of the two possible forms we are dealing with must be decided by further investigations.


A.


B.

BY WILLIAM B. CRAMER.

Orthotolylthiolmethylpseudothiourea, $(o)CH_3C_6H_4N{=}C(SCH_3)NH_2$.—Dixon[1] has recently described this pseudothiourea. We prepared the same by adding methyl iodide to orthotolylthiourea. It agreed in every respect with Dixon's body and melted at 101°. A nitrogen determination gave:

	Calculated for $C_9H_{12}N_2S$.	Found.
N	15.55	15.95

a-Orthotolyl-c-phenyl-1-thiolmethylpseudodithiobiuret, $(o)CH_3C_6H_4N{=}C(SCH_3)NHCSNHC_6H_5$.—From the action of phenyl isothiocyanate on orthotolylthiolmethylpseudothiourea in ether solution. It separated in beautiful prismatic crystals and crystallized from alcohol in magnificent plates. It was insoluble in water and melted at 114° to 115°. A nitrogen determination gave:

	Calculated for $C_{16}H_{17}N_3S_2$.	Found.
N	13.33	13.09

a-Orthotolyl-c-phenyl-1,2-thiolmethyldipseudodithiobiuret, $CH_3C_6H_4N{=}C(SCH_3)NHC(SCH_3){=}NC_6H_5$.—This base was obtained in the form of its hydriodide by warming on the steam-bath *a*-orthotolyl-*c*-phenyl-1-thiolmethylpseudodithiobiuret with the calculated quantity of methyl iodide. The hydriodide melted with effervescence at 147° to 148°. The free base was obtained by treating an alcoholic solution of the salt with sodium hydroxide. It was fairly soluble in alcohol and extremely soluble in benzene. It crystallized from alcohol in stout prisms and melted at 70° to 71°. A nitrogen determination gave:

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[1] *Loc. cit.*

	Calculated for $C_{17}H_{19}N_3S_2$.	Found.
N	12.76	13.06

a-Phenyl-c-orthotolyl-1-thiolmethylpseudodithiobiuret, $C_6H_5N=C(SCH_3)NHCSNHC_6H_4CH_3$.—This biuret was very easily obtained by combining orthotolyl isothiocyanate with phenylthiolmethylpseudothiourea. The reaction was allowed to proceed in ether solution at ordinary temperature. After evaporation of the ether there was obtained a crystalline residue, which crystallized from alcohol in plates and melted at 114° to 115°. When this pseudodithiobiuret was mixed with *a*-orthotolyl-*c*-phenyl-1-thiolmethylpseudodithiobiuret (114° to 115°) the melting-point was lowered to 100° to 103°. A nitrogen determination gave:

	Calculated for $C_{16}H_{17}N_3S_2$.	Found.
N	13.33	13.49

When the above biuret was warmed with a slight excess of methyl iodide an immediate reaction took place with formation of an addition-product. By treating this addition-product with an alcoholic solution of sodium hydroxide a base was immediately precipitated, which crystallized from alcohol in prisms and melted sharply at 70° to 71°. When this was mixed with *a*-orthotolyl-*c*-phenyl-1,2-thiolmethyldipseudodithiobiuret (m. p. 70° to 71°) the melting-point was not altered. A nitrogen determination agreed with the calculated for

$$CH_3C_6H_4N=C(SCH_3)NHC(SCH_3)=NC_6H_5.$$

	Calculated for $C_{17}H_{19}N_3S_2$.	Found.
N	12.76	12.88

a-Orthotolyl-c-phenyl-1-thiolethylpseudodithiobiuret, $CH_3.C_6H_4N=C(SC_2H_5)NHCSNHC_6H_5$.—From phenyl isothiocyanate and orthotolylthiolethylpseudothiourea. It crystallized from dilute alcohol in plates and melted at 117° to

118°. It was readily soluble in alcohol, but insoluble in water. A nitrogen determination gave:

	Calculated for $C_{17}H_{19}N_3S_2$.	Found.
N	12.76	12.50

When the above dithiobiuret was warmed on the steam-bath with 50 per cent hydrochloric acid, mercaptan was slowly given off. On cooling the acid solution, a mass of plates separated, which crystallized from alcohol in plates or thick tables and melted at 131° to 132°. A nitrogen determination agreed with the calculated for the thiolethyl ester of phenylthioallophanic acid, $C_6H_5NH.CSNHCOSC_2H_5$.

	Calculated for $C_{10}H_{12}ON_2S_2$.	Found.
N	11.66	11.65

a-Phenyl-c-orthotolyl-1-thiolethylpseudodithiobiuret, $C_6H_5N{=}C(SC_2H_5)NHCSNHC_6H_4.CH_3$.—It was necessary to allow phenylthiolethylpseudothiourea and orthotolyl isothiocyanate to stand in ether solution for several days before the reaction was complete. A thick varnish was obtained, which finally was made to crystallize by agitation in a freezing-mixture. It crystallized from alcohol in plates and melted at 95° to 96°. A nitrogen determination gave:

	Calculated for $C_{17}H_{19}N_3S_2$.	Found.
N	12.76	13.03

a,c-Diphenyl-1-thiolethylpseudodithiobiuret, $C_6H_5N{=}C(SC_2H_5)NHCSNHC_6H_5$.—From phenyl isothiocyanate and phenylthiolethylpseudothiourea. It crystallized from alcohol in plates and melted at 91° to 93°. A nitrogen determination gave:

	Calculated for $C_{16}H_{17}N_3S_2$.	Found.
N	13.33	12.99

a,c-Diorthotolyl-1-thiolethylpseudodithiobiuret, $CH_3.C_6H_4N{=}C(SC_2H_5)NHCSNHC_6H_4CH_3$. — From orthotolyl isothiocyanate and orthotolylthiolethylpseudothiourea. It crystallized from alcohol in prisms and melted at 86° to 87°. A nitrogen determination gave:

	Calculated for $C_{18}H_{21}N_3S_2$.	Found.
N	12.24	12.41

a,c-Diorthotolyl-1-thiolmethylpseudodithiobiuret, $CH_3.C_6H_4N{=}C(SCH_3)NHCSNHC_6H_4.CH_3$.—From orthotolyl isothiocyanate and orthotolylthiolmethylpseudothiourea. It crystallized from alcohol in plates and melted at 122° to 123°. A nitrogen determination gave:

	Calculated for $C_{17}H_{19}N_3S_2$.	Found.
N	12.76	13.16

New Haven, Conn.,
May 22, 1903.

Contributions from the Sheffield Laboratory of Yale University.

CIX.—ON SOME MANGANIC PERIODATES.[1]

By W. B. Price.

Although Rammelsberg[2] has asserted that periodate of manganese does not exist, I have found that the following compounds can be easily prepared:

$$Na_2Mn_2I_2O_{11};$$

$$K_2Mn_2I_2O_{11};$$

and $$H_2Mn_2I_2O_{11}.$$

These salts form beautiful, bright-red precipitates, which are exactly alike in appearance and are remarkably stable in the absence of reducing agents, since they are apparently entirely insoluble and unchanged when treated with boiling water, boiling dilute or concentrated nitric acid, and boiling dilute sulphuric acid.

The compounds are formed as exceedingly finely-divided precipitates when a solution of manganous sulphate or nitrate containing a large amount of dilute sulphuric or nitric acid is mixed with a sulphuric or nitric acid solution of sodium or potassium periodate, or, in the last case, with periodic acid. The precipitates come down after the lapse of some time in cold solutions, but rapidly upon heating to about 45°. Under

[1] Communicated by H. L. Wells.

[2] Pogg. Ann., 134, 528 (1868).

certain conditions the bright-red precipitates, when in contact with the mother-liquor, become darker in color, evidently from the formation of manganese dioxide. This decomposition is much hastened by heating above 45°, and it apparently depends upon the presence of an excess of manganous salt, which acts as a reducing agent. It is generally best, therefore, when an excess of manganese salt is used, to avoid heating more than necessary, and to separate the precipitate from the liquid by filtration as promptly as possible.

It is evident that Rammelsberg failed to get one of these compounds on account of using nearly neutral instead of strongly acid solutions.

The periodates under consideration, in containing the radical I_2O_{11}, correspond to a number of simple salts of bivalent metals which Rammelsberg prepared and called "quarter-periodates." Taking the sodium salt as an example, the formula, in terms of the oxides, is

$$Na_2O.Mn_2O_3.I_2O_7,$$

or, in terms of two assumed separate salts, it is

$$Na_8I_2O_{11}.Mn_8(I_2O_{11})_3.$$

It is certainly remarkable that compounds which are apparently so basic in their character as these should form in very acid solutions.

In examining these compounds analytically no direct test for periodates could be made, because the substances could not be dissolved without decomposing them. For determining the metals and iodine they were dissolved in sulphur dioxide solution, and the usual gravimetric methods were used. Active oxygen was determined in separate portions by treatment with potassium iodide solution and titration with nearly decinormal sodium thiosulphate. The following analyses were made:

	Calculated for $Na_2Mn_2I_2O_{11}$.	Found.		
		I.	II.	III.
Na	7.85	9.40	7.78	5.82
Mn	18.77	18.41	18.43	16.73
I	43.34	....	42.93	40.90
Active O	24.57	24.55	24.59	22.24

Sample I. was made in the presence of a very large amount of sodium salts and was probably not washed completely free from them; Sample II. was perhaps purer than the others; Sample III. was probably dried only in the desiccator, while the others were dried in a steam-oven. Hence, it seems possible that the salt as formed contains water of crystallization, which is lost at 100°, but this point was not settled.

	Calculated for $K_2Mn_2I_2O_{11}$.		Found.	
		I.	II.	III.
K	12.64	12.04	11.92	8.32
Mn	17.79	17.11	16.89	16.98
I	41.08	41.96	42.41	40.41
Active O	23.29	23.98	24.46	23.37

It should be stated that Analysis III. of both the sodium and potassium compounds, in which the alkali metal found is lower than in the others, was made with products which were probably prepared in the presence of a much greater excess of free acid than in the other cases. It appears possible, therefore, that the alkali metal may be replaced by hydrogen to some extent by the action of a large excess of acid.

The only analytical evidence which has been obtained in regard to the existence of $H_2Mn_2I_2O_{11}$ is the determination of alkalies in a substance, made from a manganous salt and periodic acid, which resembled exactly the sodium and potassium compounds. The amount of alkali-metal sulphates found was only 0.29 per cent.

NEW HAVEN, CONN., May, 1903.

Contributions from the Sheffield Laboratory of Yale University.

CX. — ON RUBIDIUM-BARIUM-SILVER THIOCYANATES.

BY HORACE L. WELLS.

The triple thiocyanates,

$Cs_3BaAg_2(SCN)_7$,
$Cs_3BaCu_2(SCN)_7$,
and $K_4BaAg_2(SCN)_8.H_2O$,

which were prepared by me last year,[1] show a disagreement in type between the caesium and potassium compounds. It was of interest, therefore, to know what similar triple compounds would be formed by rubidium, the metal intermediate between caesium and potassium.

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[1] This JOURNAL, 28, 245.

As a result of the investigation of this matter, it has been found that a rubidium-barium-silver thiocyanate,

$$Rb_4BaAg_2(SCN)_8.H_2O,$$

exists, which corresponds to the potassium salt, and that another salt,

$$Rb_2BaAg_2(SCN)_6.2(?)H_2O,$$

can be prepared. The latter is not analogous to the caesium salts, but corresponds to a type which was not previously found with barium, but which appears as the most frequently occurring type in the salts,

$$Cs_2CaAg_2(SCN)_6.2H_2O,$$
$$Cs_2MgAg_2(SCN)_6.2H_2O,$$
$$Cs_2MnAg_2(SCN)_6.2H_2O,$$
$$Cs_2NiAg_2(SCN)_6.2H_2O,$$
$$Cs_2NiCu_2(SCN)_6.2H_2O,$$
$$Cs_2CoAg_2(SCN)_6.2H_2O,$$
$$Cs_2CdAg_2(SCN)_6.2H_2O,$$

and $Cs_2CdAg_2(SCN)_6$.

The two rubidium salts under consideration are very soluble, crystallize poorly, and hence are difficult to produce in a satisfactory condition. They were prepared under practically the same conditions, and it is not known what is the cause of the appearance of one instead of the other in a solution.

Attempts to make a rubidium-barium-cuprous thiocyanate were entirely unsuccessful, for appropriate solutions for preparing such a compound evaporated over sulphuric acid to transparent, solid masses without showing signs of crystallization.

4 : 1 : 2, Rubidium-Barium-Silver Thiocyanate, $Rb_4BaAg_2(SCN)_8.H_2O$.—A solution containing rubidium, barium, and silver thiocyanates in the molecular proportion 3 : 1 : 2 was evaporated over sulphuric acid. When the liquid had become very dense a product was formed which was too unsatisfactorily crystallized to be used for analysis. After a considerable quantity of it had formed, therefore, it was drained as far as possible from the thick mother-liquor by suction on a platinum cone, and then it was dissolved in water and the solution was evaporated over sulphuric acid. This solution did not form good crystals readily, but after repeated trials a crop of large, transparent, prismatic crystals was obtained. These crystals were not well formed and their crystalline form was not determined. No other crop of this salt could be obtained, although several attempts were made to get it; hence the evidence of its existence is confined to the analysis of the single crop, but the correspondence of the composition to that of the potassium salt considerably strengthens the evidence. The results of the analysis are as follows:

	Calculated for $Rb_4BaAg_2(SCN)_6.H_2O$.	Found.
Rb	29.02	....
Ba	11.68	12.36
AgSCN	28.20	28.20
Sol. SCN	29.57	29.30
H_2O	1.53	1.25

2 : 1 : 2, Rubidium-Barium-Silver Thiocyanate, $Rb_2BaAg_2(SCN)_6.2(?)H_2O$.—When attempts were made to prepare other crops of the 4 : 1 : 2 salt under the same and considerably varying conditions, in respect to the mixtures used, and when recrystallizations were made of the first crude crops as in the case described, three fairly satisfactory crops were obtained, but they showed a composition entirely different from the original one. There is doubt about the amount of water in this compound, for the crops, when well pressed upon filter-paper, became very wet when preserved in a corked tube and needed to be dried again before they were analyzed, and when air-dried the substance became somewhat opaque, evidently from loss of water. About 1 molecule of water, or somewhat less, remained in the samples, but since some water had been lost, it is assumed from analogy with other salts of this type that the original amount of water was probably 2 molecules. The crops were not well crystallized, but they appeared to be homogeneous.

The following analyses were made with air-dry samples. The calculation is made for 1 molecule of water, since this was approximately the amount present:

	Calculated for $Rb_2BaAg_2(SCN)_6.H_2O$.	Found.		
		I.	II.	III.
Rb	19.19	....	....	....
Ba	15.45	13.88	14.61	13.49
AgSCN	37.29	36.07	36.68	37.11
Sol. SCN	26.06	26.06	26.16	25.98
H_2O	2.02	2.32	1.01	1.57

NEW HAVEN, CONN., May, 1903.

THE VOLUMETRIC DETERMINATION OF MERCURY AND OF HYDROCYANIC ACID.

BY LAUNCELOT W. ANDREWS.

It is a familiar fact that hydrocyanic acid is a "pseudo-acid" which possesses no acid reaction at all toward many indicators, as methyl orange, nitrophenol, etc., and which cannot be acidimetrically titrated even with the aid of extremely acid-sensitive indicators, such as phenolphthalein or toluylene-red. If silver nitrate is added to a solution of hydrocyanic acid a quantitative precipitation of silver cyanide occurs, and if the silver salt is in excess, an amount of nitric acid is set free equivalent to the hydrocyanic acid used. Titration of the nitric acid by the aid of any suitable indicator, such as paranitrophenol, leads to a knowledge of the amount of hydrocyanic acid originally present. The process is accurate but not especially convenient. The precipitated silver cyanide may retain free hydrocyanic acid or silver nitrate, or both, according to the conditions of the precipitation, semipermeable "cells" being formed which give up their contents very slowly by long-continued washing, and which continue to exhibit an acid reaction even after washing with excessive amounts of water. This difficulty can be brought within bounds by precipitating from highly dilute solutions. It might be thought possible to titrate the free nitric acid directly, without filtering from the precipitate, and such is in fact the best mode of proceeding. Nitrophenol is a good indicator for the purpose, although methyl orange may be used. Lacmoid forms an insoluble compound (silver salt?) which disturbs the sharpness of the end-reaction. If the hydrocyanic acid is in excess and silver nitrate from a known amount of metallic silver is employed, an exactly determinate quantity of nitric acid will be set free, and, hence, the titration can be used for the standardizing of acidimetric alkali solutions, the object with which the experiments were originally undertaken. The advantage of using pure metallic silver as the standard is obvious, but the difficulties referred to above, lying in the character of the precipitate, appear here also, in an aggravated form. The attempt to titrate the free nitric acid without filtering from the silver cyanide meets with almost insuperable difficulties when the solution contains an excess of hydrocyanic acid.

In this case, as soon as the free nitric acid is neutralized, the complex salt, potassium argentocyanide, $KAgCy_2$, begins to form in accordance with the reaction

$$HCN + AgCN + KOH = KAg(CN)_2 + H_2O.$$

Potassium argentocyanide is a neutral salt, so that the reaction of the solution changes from acid to neutral as excess of potassium hydroxide is added, instead of from acid to alkaline, and remains neutral until all hydrocyanic acid is converted into potassium argentocyanide. At the same time, the silver nitrate occluded in the precipitate slowly diffuses out, reacting as it does so with the hydrocyanic acid. It is therefore necessary to filter before titrating, and previous to the filtration a digestion for at least twenty-four hours is necessary, during which time the precipitate must be agitated with the solution. It is not thought worth while to give the details of the long series of experiments, since the final result is that the method, while capable of a high degree of accuracy when all precautions are observed, does not possess the simplicity which can be demanded of such a process.

It appeared to the writer to be a question as to how far the completeness of the reaction between hydrocyanic acid and silver nitrate is due to the insolubility of silver cyanide, and how far to its being, possibly, a compound not subject to electrolytic dissociation, that is, not a true salt at all. If the latter were the dominant factor, it should be possible to secure a practically complete reaction between mercuric nitrate or chloride and hydrocyanic acid, since mercuric cyanide is well known to be a non-dissociated compound. If methyl orange is added in small quantity to a solution of pure mercuric chloride and also to a solution of hydrocyanic acid, both solutions remain pure yellow, showing no trace of acid reaction. If the solutions are now mixed together, they turn bright-red. The experiment makes a striking lecture experiment illustrative of the theory of electrolytic dissociation. Nitrophenol, lacmoid paper, or even a rather insensitive, strongly blue, litmus paper can be used instead of methyl orange to show the liberation of hydrochloric acid, *i. e.*, the production of hydrogen ions. The reaction,

$$HgCl_2 + 2HCN = Hg(CN)_2 + 2HCl,$$

is not instantaneous, but is practically complete, and the disturbing factors mentioned above as occurring in the reaction between silver salts and hydrocyanic acid, are absent. It appears, therefore, probable that silver cyanide also is a non-dissociated compound, and that the so-called "elective affinity" between cyanogen and silver is a phenomenon due to this fact rather than to the low solubility of silver cyanide, a supposition with which the known fact that an alkali cyanide reacts quantitatively with silver chloride to form silver cyanide is in the best of harmony.

The possibility of the application of these relationships to the acidimetric titration of mercury or of hydrocyanic acid and the cyanides lies very near. In the sequel it is shown that the possibility can easily be realized. It may be said that no new method for the titration of hydrocyanic acid is needed, since that of Liebig,[1] as modified by Denigés,[2] answers all practical requirements. It is to be noted, however, that the application of Liebig's method requires a perfectly clear solution, whereas pharmaceutical preparations of hydrocyanic acid are frequently turbid. The addition of a new and convenient method of titration to the small number of those already known for the determination of mercury cannot be regarded as a work of supererogation, especially when the new method, as is the case with that described, is applicable to the determination of mercuric chloride in the highly dilute solutions of that substance employed by surgeons.

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[1] Ann. Chem. (Liebig), 77, 102 (1851).

[2] Ann. chim. phys. [7], 6, 381 (1895).

Determination of Hydrocyanic Acid and Cyanides.

For this determination the following solutions are required: *a*, decinormal solutions of hydrochloric acid and of potassium (or sodium) hydroxide; *b*, a nearly saturated solution of mercuric chloride, containing about 40 grams of the pure recrystallized salt per liter. The exact strength of this solution need not be known; *c*, a saturated solution of pure paranitrophenol in water. This is to be preferred to the solution in alcohol often recommended as an indicator. The aqueous solution keeps indefinitely in the light or in the dark.

To determine hydrocyanic acid or a simple cyanide, dilute the solution till it contains not more than about 1 per cent of hydrocyanic acid and add 2 drops of nitrophenol solution. If this imparts a yellow color, add decinormal hydrochloric acid until the color has all but disappeared; if it is colorless, add decinormal potassium hydroxide till the solution shows a very pale yellow. Now, add an excess of the mercuric chloride solution (usually 15 or 20 cc.), stir and allow to stand for one hour at the temperature of the air.

A solution of hydrocyanic acid which had by gravimetric analysis been found to contain 3.40 per cent, was analyzed by the above method. For that purpose, 50 cc. was measured by a pipette into a 500 cc. flask, filled to the mark, and shaken. Five cc. of this solution were mixed with 10 cc. of an approximately decinormal mercuric chloride solution, allowed to stand for an hour, and then titrated as described. Required, 6.30 cc. of N/10 KOH, equivalent to 0.01704 gram of hydrocyanic acid, or 3.408 per cent found.

Twenty cc. of the same solution were mixed with 10 cc. of an approximately 4 per cent mercuric chloride solution and the liquid allowed to stand three hours. Required, 25.03 cc. of decinormal potassium hydroxide, equivalent to 0.0677 gram of hydrocyanic acid or 3.385 per cent (on original solution) found.

From the original solution was prepared, by suitable dilution, a semi-normal hydrocyanic acid solution, containing, by calculation, 13.52 grams per liter. Five cc. of this solution were mixed with 33 cc. of the last-mentioned mercuric chloride solution, and, after standing fifteen minutes, were titrated in the usual way. Required, 24.78 cc. of decinormal potassium hydroxide, equivalent to 0.06703 gram of hydrocyanic acid or 1.34 per cent found. The small deficit observed here is probably due to a slight volatilization of hydrocyanic acid during the manipulations incidental to dilution and exposure.

Determination of Mercury.

The only solution required, in addition to those mentioned above, is an approximately normal solution of hydrocyanic acid neutral to nitrophenol. Such a solution may be conveniently prepared in the following way without distillation: Dissolve 68 to 80 grams of the best commercial potassium cyanide in 0.5 liter of water, add about 5 grams of barium chloride in saturated solution, and filter, thus removing carbonates which would interfere with the exact neutralization. To the filtrate add about 10 cc. of the nitrophenol solution (*vide supra*), and then dilute sulphuric acid till the yellow color has become pale, finishing the neutralization with decinormal hydrochloric acid. Finally, make up to a liter, disregarding the barium sulphate which may be allowed to subside. This solution should contain about 27 grams of hydrocyanic acid and be colorless.

The mercury to be determined must be present as mercuric chloride (or bromide?). If in the form of nitrate, a small excess of sodium chloride is added. Organic acids must be absent. It is next to be made neutral by addition of nitrophenol, avoiding undue excess, and hydrochloric acid till the yellow color is just on the point of disappearing. To the solution so prepared an excess of the neutral hydrocyanic acid solution is added and the mixture set aside for not less than one hour for the completion of the reaction. The hydrochloric acid formed is titrated with potassium hydroxide, decinormal or centinormal, according to the dilution of the mercuric solution, until a permanent pale-yellow tint is visible. A very small excess of hydrocyanic acid suffices, and an unnecessary excess is for obvious reasons to be avoided. To be sure that sufficient hydrocyanic acid is present, if in doubt, add a few drops at the conclusion of the titration. This will instantly destroy the yellow color if insufficient had been present, but otherwise will not affect it. The method has been repeatedly used by students in this laboratory with very satisfactory results, in part for the determination of mercuric chloride in solutions containing one part in ten thousand. They have with it obtained much better results than by the method of Vitali[1] for the examinatlon of dilute solutions, and in considerably less time. Vitali's method consists in boiling the mercuric chloride solution with an excess of sulphurous acid, expelling the excess, and titrating acidimetrically the sulphuric and hydrochloric acids formed. The method is satisfactory for stronger solutions of mercuric chloride, but certain sources of error which are inappreciable in concentrated solution become serious when the solution is highly dilute. These are oxidation of the sulphurous acid by the atmosphere, imperfect expulsion of the last traces of sulphurous acid, reduction of the mercury too far, *i. e.*, to metal. Prolonged boiling is needed to drive off the last of the sulphur dioxide, which passes off rapidly at first, but with extreme slowness when only a little is left. Reduction of the mercurous chloride to metal is hindered by the considerable amount of hydrochloric acid present in more concentrated solutions, but in those of high dilution the amount of acid is insufficient to have this effect. The precipitate in the latter

[1] Bolletino Chimico Farmaceutico, 1894, 365.

case often becomes gray. All these sources of error lead to the results of the determination being too high.

That the cyanide method also gives correct results with more concentrated solutions is shown by the following test analyses:

A solution was prepared containing 6.780 grams of pure mercuric chloride in 500 cc. It was perfectly neutral to nitrophenol. To 5 cc. of it, 2 cc. of a hydrocyanic acid solution (3.4 per cent) was added, and 1 drop of nitrophenol solution. Required, 5 cc. of decinormal potassium hydroxide, equivalent to 0.0678 gram found. Twenty-five cc. of the same solution, with 5 cc. of hydrocyanic acid, required 25 cc. of the standard alkali, equivalent to 0.339 gram of mercuric chloride found. Again, 25 cc. of the same solution, with 10 cc. of hydrocyanic acid and 100 cc. of water, required 25.03 cc. of the hydroxide, equivalent to 0.3394 gram of mercuric chloride found.

Since mercuric chloride is a substance which can be easily obtained in a high state of purity and is in every way well defined, it is suited as a standard for acidimetric solutions, the sharpness of the method of titration which has been described making it readily available for this purpose.

The results quoted of themselves show the practicability of this method, of which I shall have something more to say in connection with a discussion of other methods of standardization.

CHEMICAL LABORATORY,
STATE UNIV. OF IOWA,
May 16, 1903.

THE ASSOCIATION OF A LIQUID DIMINISHED BY THE PRESENCE OF ANOTHER ASSOCIATED LIQUID.

BY HARRY C. JONES AND GRANTLAND MURRAY.

Ramsay and Shields,[1] in their beautiful investigation on the surface-tension of liquids, showed conclusively that the molecules of certain liquids are made up of a number of the simplest molecules, while the molecules of other liquids are identical with the simple chemical molecule. They pointed out that if we represent the degree of association, or the association factor, by x, that

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[1] Ztschr. phys. Chem., **12**, 433 (1893).

$$x^{\frac{2}{3}} = \frac{2.12}{k},$$

in which k, the differential coefficient for the liquid between any two known temperatures, can be calculated by measuring the surface-tension of the liquid at the temperatures in question, knowing the molecular volume at these temperatures.

If the liquid is not associated the value of this coefficient is 2.12. If the liquid is associated the value of the coefficient k is always less than 2.12, and the association factor, x, or number of molecules associated to form the molecule of the liquid, can be calculated thus :

$$x = \left(\frac{2.12}{k}\right)^{\frac{3}{2}}.$$

Ramsay and Shields showed that of the common liquids water has the highest association factor, its molecule at 0° being made up of 4 molecules of the composition H_2O, or has the composition $(H_2O)_4$. The alcohols of the methyl alcohol series are also strongly associated liquids, especially the first members of the series, and the same holds for the formic acid series of acids ; formic and acetic acids being especially strongly aggregated compounds.

The above investigation acquired a new interest when Dutoit and Aston[1] pointed out that there is a connection between the association of any solvent and its own dissociating power. It was made probable that only those liquids whose molecules are polymerized or associated have the power of breaking down or dissociating the molecules of electrolytes into ions. This relation is obvious in the case of water, which is the most highly associated liquid, and which, of all the common solvents, has the greatest ionizing power.

The present investigation was undertaken with the object of determining the effect of one associated liquid on the association of another associated liquid. This line of work was suggested by an investigation[1] which was carried on in this laboratory last year. The investigation in question had to do with the relation between the conductivity of salts in water, methyl, ethyl, and propyl alcohols, and in mixtures of these solvents. It was found that the conductivity of the salt in the mixed solvents was very frequently less, for a given concentration, than in the lower conducting of the two solvents present in the mixture. This was established in mixtures of methyl alcohol and water for a number of salts, such as potassium iodide, ammonium bromide, strontium iodide, and lithium nitrate, the salt conducting less in the mixture of methyl alcohol and water than in pure methyl alcohol. Ethyl alcohol and water at 0° showed a similar phenomenon for all the salts investigated.

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[1] Compt. rend., **125**, 240 (1897).

Salts dissolved in a mixture of equal parts of methyl and ethyl alcohols do not conduct less than in pure ethyl alcohol, but show a conductivity which is less than the mean of the conductivities of the substances in the pure solvents at the same dilution. This is obviously a result of the same general character as that obtained with mixtures of the alcohols and water. This investigation was extended to a number of mixtures of the different solvents at different temperatures, and the concentrations of the solutions of salts which were employed were varied greatly. The results were of the character indicated.

At first sight it was extremely difficult, not to say impossible, to interpret these results. How could an electrolyte in a mixture of methyl alcohol and water be dissociated less than in pure methyl alcohol, when water had a much higher dissociating power than methyl alcohol? This could be explained most easily on the assumption that each solvent so acted on the other as to diminish its dissociating power, and this suggestion[2] was made as a possible explanation of the results.

At the time the suggestion was made the evidence bearing upon the case was very meagre indeed. It was known that methyl and ethyl alcohols, whose molecules in the pure, homogeneous liquids are considerably aggregated, give normal molecular weights when dissolved in water.[1] This evidence, however, was far from sufficient to justify any general conclusion on the subject. In order to determine whether associated liquids have any general influence on each other's association, it is necessary to take associated liquids and determine the molecular weights of each in the other, and then compare the results with the molecular weights of the several liquids in the pure condition.

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[1] Jones and Lindsay: This JOURNAL, **28**, 329 (1902).

[2] Lindsay: *Ibid.*, **28**, 369 (1902).

There are not many liquids which can be employed in this work, since the boiling-point method of determining molecular weights cannot be used for any liquid dissolved in another liquid. We are, therefore, limited to the freezing-point method, and of those liquids whose association is known, only a few freeze at temperatures to which the freezing-point method can be applied.

Liquids Used in this Work.

We have found three liquids which fulfil in an admirable manner the conditions necessary for this work, *i. e.*, they must dissolve readily in one another, must not act chemically upon one another, must not undergo appreciable electrolytic dissociation, and must be strongly associated substances. These liquids are water, acetic acid, and formic acid.

Purification of the Liquids.

The water used in this investigation was purified by double distillation. It was first distilled from chromic acid, which destroyed the organic matter and retained the ammonia, and then from barium hydroxide, which retained the carbon dioxide. Its conductivity was 1.2×10^{-6}.

The acetic acid was furnished by Bender and Hobein for cryoscopic work. This was fractionally crystallized, using a large volume at the outset and discarding about half at each crystallization. After the freezing-point showed that the material was nearly pure, a relatively smaller amount was discarded at each crystallization. After ten crystallizations a specimen was obtained which froze sharply at 16°.5, and which was, therefore, practically pure acetic acid.

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[1] Jones: Ztschr. phys. Chem., **12**, 623 (1893).

It was found to be much more difficult to obtain formic acid free from water. The purest specimen that could be purchased was treated with a large amount of phosphorus pentoxide and distilled. The formic acid was decomposed to some extent by the pentoxide into carbon monoxide and water, but the amount of water removed in this way was very much greater than the amount formed as the result of the decomposition of the acid. The product resulting from the distillation was then subjected to fractional crystallization. After freezing out the acid fifteen or twenty times, discarding in each case a considerable volume, a product was obtained which froze at 7°. *The statement in the literature that formic acid freezes below zero and melts at 8°.5 is, therefore, erroneous.* The specimen which fulfilled these conditions must have contained considerable water. Such a specimen would freeze only when cooled considerably below its melting-point, and the crystals which separated, being comparatively free from water, would then melt close to the true melting-point of the acid.

With the above liquids the following measurements were made by the freezing-point method :

I. The molecular weight of water in acetic acid.
II. The molecular weight of water in formic acid.
III. The molecular weight of acetic acid in water.
IV. The molecular weight of acetic acid in formic acid.
V. The molecular weight of formic acid in water.
VI. The molecular weight of formic acid in acetic acid.

Results.

The results are given in the following tables. Column I. contains the amount of solvent used ; Column II. the amount of liquid whose molecular weight was to be determined ; Column III. the concentration in terms of normal, a normal solution being defined as one that contains a gram-molecular weight of the electrolyte in 1,000 grams of the solvent ; Column IV. gives the freezing-point lowerings actually observed ;

and Column V. the molecular weight of the liquid at the concentration in question. In all of this work care was taken to keep the temperature of the freezing-mixture only a little below the freezing-point of the solution.

Water (18) in Acetic Acid.

I.	II.	III.	IV.	V.
Acetic acid.	Water.	Concentration.	Lowering.	Molecular weight.
39.68	0.454	0.64	2°.06	21.7
38.32	0.514	0.75	2°.38	22.0
"	0.820	1.19	3°.58	23.3
39.68	0.947	1.33	3°.93	23.7
"	1.547	2.17	5°.89	25.8
"	2.061	2.89	7°.45	27.2
"	2.541	3.56	8°.79	28.4
38.32	2.637	3.82	9°.33	28.8
39.68	2.992	4.19	9°.95	29.6
"	3.870	5.42	12°.11	31.4
"	4.686	6.56	14°.00	32.9
"	5.589	7.83	16°.04	34.2
"	6.472	9.06	17°.86	35.6
"	7.566	10.59	20°.07	37.1
"	8.559	11.98	22°.00	38.2
"	9.032	12.65	22°.90	38.8

Water (18) in Formic Acid.

I.	II.	III.	IV.	V.
Formic acid.	Water.	Concentration.	Lowering.	Molecular weight.
48.24	0.808	0.93	2°.35	19.7
"	1.325	1.53	3°.75	20.3
"	2.204	2.54	6°.13	20.6
"	3.060	3.52	8°.30	21.2
"	4.434	5.13	11°.69	21.8
"	5.376	6.18	14°.11	21.9

Acetic Acid (60) in Water.

I.	II.	III.	IV.	V.
Water.	Acetic acid.	Concentration.	Lowering.	Molecular weight.
37.15	0.376	0.17	0°.34	55.4
"	3.959	1.78	3°.30	60.1
"	6.830	3.06	5°.45	62.7
50.65	10.794	3.56	6°.19	64.0
62.17	17.474	4.70	7°.85	66.6
37.15	10.771	4.83	8°.05	67.0
37.15	15.728	7.06	10°.92	72.1

Acetic Acid (60) in Formic Acid.

I. Formic acid.	II. Acetic acid.	III. Concentration.	IV. Lowering.	V. Molecular weight.
40.35	0.433	0.18	0°.48	61.9
34.23	1.018	0.50	1°.27	64.9
40.35	1.593	0.66	1°.65	66.3
34.72	1.835	0.88	2°.16	67.8
34.23	2.256	1.10	2°.67	68.4
38.49	2.873	1.24	2°.98	69.4
34.72	3.968	1.90	4°.45	71.1
38.49	6.464	2.80	6°.29	74.0
34.72	10.708	5.14	10°.97	77.9
34.23	10.764	5.24	11°.16	78.0
"	18.838	9.17	18°.19	83.8

Formic Acid (46) in Water.

I. Water.	II. Formic acid.	III. Concentration.	IV. Lowering.	V. Molecular weight.
35.10	0.546	0.34	0°.64	45.2
193.67	7.850	0.88	1°.62	46.5
35.10	1.667	1.03	1°.89	46.7
"	4.928	3.05	5°.28	49.5
136.79	31.564	5.03	8°.50	50.5
141.43	40.109	6.16	10°.34	51.0

Formic Acid (46) in Acetic Acid.

I. Acetic acid.	II. Formic acid.	III. Concentration.	IV. Lowering.	V. Molecular weight.
30.41	1.152	0.82	2°.93	50.4
"	1.702	1.22	4°.26	51.2
"	2.303	1.65	5°.66	52.2
"	2.820	2.02	6°.84	52.9
"	3.410	2.44	8°.10	54.0
"	4.267	3.05	9°.93	55.1
"	5.098	3.64	11°.55	56.6
"	6.136	4.39	13°.53	58.2
"	7.024	5.02	15°.24	59.1
50.64	14.814	6.36	18°.40	62.0
30.02	11.403	8.26	22°.54	65.7

These results are plotted in curves. The molecular weight of water in acetic acid and formic acid with varying concentration in Fig. I., the molecular weight of acetic acid in water and in formic acid in Fig. II., and the molecular weight of formic acid in water and in acetic acid in Fig. III.

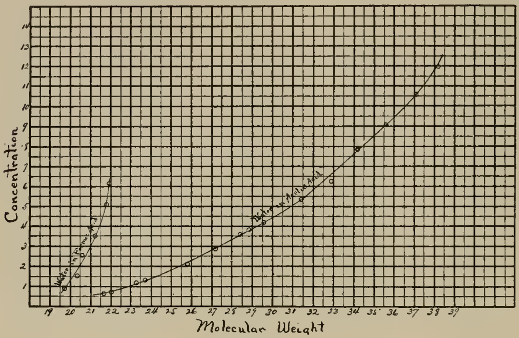

Fig. I.

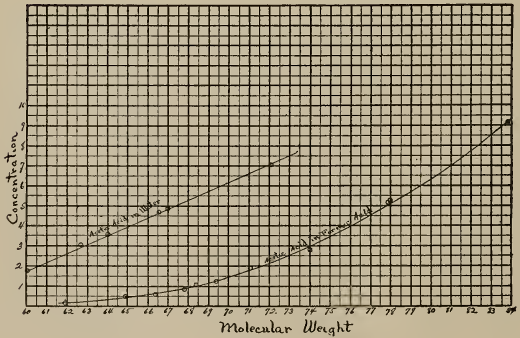

Fig. II.

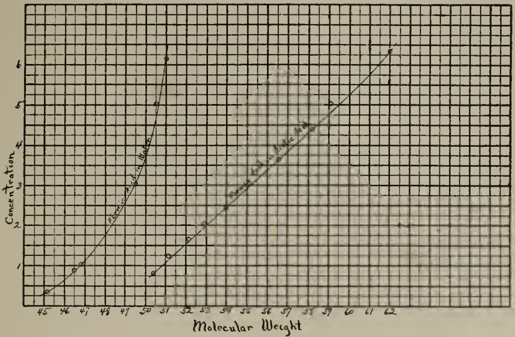

Fig. III.

Discussion of Results.

The molecular weight of water in acetic acid at the greatest dilution used (0.64 normal) is 21.7, which is only slightly greater than the molecular weight corresponding to the composition H_2O. In the most concentrated solution used, which is somewhat more than twelve times normal, the molecular weight of the water is a little more than would correspond to the composition $(H_2O)_2$. In pure water, however, we know, from the work of Ramsay and Shields, that the molecules have the composition $(H_2O)_4$. The association of water is, therefore, greatly diminished by the presence of the associated solvent, acetic acid.

The same remarks apply to solutions of water in formic acid. At the greatest dilution, the molecular weight of the water is only slightly above normal, the molecular weight increasing slightly as the concentration of the solution increases. The complex molecules of water are broken down to even a greater extent by formic acid than by acetic acid. This is in keeping with the relative powers of these two solvents to break molecules down into ions, formic acid being a much stronger dissociant than acetic acid.

The molecular weight of acetic acid in water is approximately normal for the more dilute solutions investigated, increasing somewhat above normal in the more concentrated solutions. The amount of electrolytic dissociation of even the most dilute solutions of acetic acid in water is so small as to exercise only a slight influence on the results.

Pure acetic acid, at the freezing temperature, is a very much associated liquid. The work of Ramsay and Shields[1] has shown that the differential coefficient *k* for acetic acid between 16° and 46°, is 0.9. The association

$$x = \left(\frac{2.12}{0.9}\right)^{\frac{3}{2}} = 3.6.$$

It is, therefore, obvious that the association of acetic acid is greatly diminished by water.

The molecular weight of acetic acid in formic acid is greater than in water at the same concentrations, ranging from 61.9 to 83.8 for the different concentrations employed. This, again, is what we might expect. Water having a greater power than formic acid to break molecules down into ions, also has a greater power to break down complex molecules into simpler ones. In no case, however, is the molecular weight of acetic acid in formic acid greater than about one and one-fourth the simplest molecular weight, showing that the complex molecules of pure acetic acid are greatly decomposed by the formic acid.

The same remarks apply, in general, for formic acid in water and in acetic acid. Formic acid, in the pure condition, is associated to just about the same extent as acetic acid. Ramsay and Shields[2] found the coefficient *k* for formic acid to be 0.902. Therefore, the association is,

$$x = \left(\frac{2.12}{0.902}\right)^{\frac{3}{2}} = 3.6.$$

The molecular weight of formic acid in water is only slightly greater than normal, even at the greatest concentration employed. In acetic acid the molecular weight is greater than in water at the same concentration. This is analogous to what has been found with the other solvents employed. Water has the greater power to break down molecules into ions, and also the greater power to decompose molecular complexes into simpler molecules.

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[1] Ztschr. phys. Chem., **12**, 469 (1893).

[2] *Ibid.*, **12**, 469 (1903).

Effect of the Dissolved Substance on the Constant of the Solvent.

The above results show that the associated molecules of the dissolved substance are broken down by the solvent into simpler molecules. It is also true that the molecules of the solvent are broken down into simpler molecules by the molecules of the dissolved substance. The magnitude of this influence will depend upon the concentration of the solution and the state of aggregation of the dissolved substance in the solution. It is not a simple matter to determine the exact magnitude of the effect on the solvent, which will be produced in any given case.

In the calculation of the molecular weights of the dissolved substances, given above, the freezing-point constant of the solvent is assumed to be constant. Since the dissolved liquid diminishes the association of the solvent, it will, from Raoult's law, diminish the freezing-point constant of the solvent. This effect will become appreciable only when the concentration of the solution has become considerable. As the freezing-point constant becomes less the molecular weight as calculated from the observed freezing-point lowering would be less than that given above. The effect of this influence of the dissolved substance on the solvent would, then, be to give still smaller molecular weights for the former than those calculated above, especially for the more concentrated solutions. In a word, to show a still greater diminishing of the association of the dissolved substance by the solvent than would be indicated by the above results. This would change somewhat the position of the curves, especially in the more concentrated solutions, but in such a way as to augment the effect, which is shown so clearly by them.

Further, in the more concentrated solutions it is not at all certain that the pure solid phase of the solvent separated from the solution. This may have been mixed with the solid phase of the liquid present in the smaller quantity. The result would have been to give a smaller lowering of the freezing-point, and, consequently, a higher molecular weight for the dissolved substance.

Since both of the above effects manifest themselves to an appreciable extent only in the more concentrated solutions, the results, as found experimentally in the more dilute solutions, may be regarded as very close to the true molecular weights of the several liquids when dissolved in one another. In the more concentrated solutions the true molecular weights are smaller than those found by experiment. The latter show a very marked diminution in the complexity of the molecule in solution, as compared with the pure state. This would be still more obvious if the exact molecular weight of the dissolved liquid in concentrated solutions could be determined.

Explanation of the Results Obtained by Jones and Lindsay.

In the light of the above facts the results obtained by Jones and Lindsay are easily explained. An electrolyte conducts less in a mixture of methyl alcohol and water because these two strongly associated solvents diminish each other's association, and, since each diminishes the association of the other, it diminishes the dissociating power of the other solvent. The dissociation of an electrolyte in the mixed solvents is less than in the lower dissociating solvent, and, consequently, the conductivity is less in the mixed solvents.

The position of the minimum in the curve expressing the relation between molecular conductivity and concentration of alcohol in the mixed solvents can be also readily interpreted, now that we know the effect of one associated solvent on the association of another associated solvent.

The minimum conductivity shown by a solution of an electrolyte of given concentration, in mixtures of water and alcohol, corresponds to that particular mixture of alcohol and water which has the least dissociating power. This is the same as to say, to that particular mixture of alcohol and water in which, at the temperature in question, the association of each solvent is at a minimum. This mixture, at which the minimum conductivity occurs, is the particular mixture of the two solvents in which each has diminished the association of the other to a maximum extent.

It is worthy of note that the position of the minimum changes with change in temperature, occurring at the more elevated temperature in the mixture of alcohol and water containing more alcohol. This may have to do with the fact that the critical temperature, or the temperature at which all association disappears, is less for methyl, ethyl, and propyl alcohols than for pure water. Therefore, the effect of a given rise in temperature would probably be to decrease the association of the alcohols more than that of water. This influence would add itself to that resulting from the effect of each of the solvents on the association of the other, and would show the minimum dissociation, and, consequently, the minimum conductivity in the region where there was more alcohol and less water present. This seems to us to be a possible explanation of the otherwise unexplained fact that the minimum in the conductivity curve is shifted with change in temperature.

We propose to extend this investigation, especially to the action of non-associated solvents on the association of associated solvents.

Chemical Laboratory,
Johns Hopkins Univ.,
April, 1903.

THE LOWERING OF THE FREEZING-POINT OF AQUEOUS HYDROGEN DIOXIDE BY SULPHURIC AND ACETIC ACIDS.

By Harry C. Jones and Grantland Murray.

The lowering of the freezing-point of aqueous hydrogen dioxide, produced by certain salts, was first measured in this laboratory about two years ago.[1] The salts that were studied were potassium chloride, sodium nitrate, and potassium nitrate. The lowering of the freezing-point of aqueous hydrogen dioxide was compared with the lowering of the freezing-point of water produced by these same substances, with the result that they were found to lower the freezing-point of water to a greater extent than the freezing-point of the dioxide.

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[1] Jones, Barnes, and Hyde : This Journal, **27**, 22 (1902).

The work begun by Jones, Barnes, and Hyde was extended by Jones and Carroll[1] to ammonium sulphate and also to sulphuric and oxalic acids. Results were obtained with ammonium sulphate which were of the same general character as those yielded by the salts earlier investigated. Ammonium sulphate lowered the freezing-point of water to a greater extent than the freezing-point of hydrogen dioxide.

The results with sulphuric and oxalic acids were quite different from those obtained with salts. The acids produced a greater lowering of the freezing-point of the dioxide than of water. Only a few measurements, however, were made with the acids, and the object of the present investigation was to repeat and extend the earlier work in this field.

We have worked with sulphuric acid, which is strongly dissociated, and with acetic acid which is only slightly dissociated. The hydrogen dioxide was purified exactly as in the earlier work. The sulphuric acid was added slowly to the aqueous solution of the dioxide, which was kept surrounded by ice to prevent the temperature from rising appreciably. The concentration of not only the original hydrogen dioxide was ascertained, but also the concentration of the dioxide after the sulphuric acid had been added, and the freezing-point of the solution determined. The strength of the aqueous solution of hydrogen dioxide was always ascertained by titrating against a standard solution of potassium permanganate.

The Results with Sulphuric Acid.

The sulphuric acid which was employed was only 96 per cent H_2SO_4. The corresponding correction for the 4 per cent of water was introduced.

The change in the concentration of the solution, due to the separation of ice from the undercooled liquid, was corrected, taking into account the effect of the presence of both hydrogen dioxide and sulphuric acid.

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[1] This JOURNAL, **28**, 284 (1902).

In the following tables, Column I. gives the percentage concentration of the hydrogen dioxide; Column II. the concentration of the sulphuric acid in terms of gram-molecules per liter; Column III. the corrected lowering of the freezing-point; and Column IV. the molecular lowering of the freezing-point.

The results[1] with sulphuric acid and water are:

II.	III.	IV.
1.0	4°.190	4°.190
0.5	2°.030	4°.060
0.3	1°.173	3°.910
0.1	0°.396	3°.960

The following results were obtained with sulphuric acid in aqueous hydrogen dioxide:

I.	II.	III.	IV.
4.64	1.209	6°.263	5°.18
4.74	0.710	3°.311	4°.66
4.77	0.511	2°.293	4°.49
4.84	0.337	1°.490	4°.41
9.34	0.771	4°.263	5°.53
8.84	0.680	3°.757	5°.52
9.00	0.519	2°.838	5°.47
9.53	0.484	2°.526	5°.22
10.19	0.470	2°.432	5°.14
8.83	0.328	1°.630	4°.97
9.15	0.242	1°.165	4°.81
9.73	0.138	0°.717	5°.19

These results are of the same general character as those obtained by Jones and Carroll. The freezing-point of hydrogen dioxide is lowered to a much greater extent by sulphuric acid than the freezing-point of water, and just as we would expect, the molecular lowering is greater the more concentrated the solution of hydrogen dioxide.

The Results with Acetic Acid.

The acetic acid was prepared by fractionally crystallizing the purest specimen which could be obtained commercially, until the melting-point showed that practically all the water had been removed. The same precautions and corrections were introduced with the acetic acid as with sulphuric acid. The change in the concentration of the hydrogen dioxide, produced by the addition of the acetic acid, and the change in concentration due to undercooling, were taken into account and the corresponding corrections applied. The lowering of the freezing-point of water by acetic acid was determined, and the following results obtained :

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[1] Jones and Carroll: This Journal, 28, 291 (1902).

II.	III.	IV.
4.251	8°.80	2°.07
2.715	5°.40	1°.99
2.121	4°.176	1°.97
1.358	2°.592	1°.91
1.063	2°.020	1°.90
0.530	1°.000	1°.89
0.266	0°.507	1°.91
0.133	0°.276	2°.08
0.0665	0°.140	2°.11

The lowering of the freezing-point of water produced by acetic acid is about what we would expect from its small dissociation, and the minimum in the molecular lowering, calculated on the above basis, is analogous to what was found by Jones and Getman[1] for such a large number of electrolytes.

The following results were obtained with acetic acid in aqueous hydrogen dioxide of varying concentration. Two series of measurements were made, in which the strengths of both the hydrogen dioxide and the acetic acid were varied. The results are given below :

I.	II.	III.	IV.
3.57	4.186	8°.869	2°.12
3.75	2.093	4°.241	2°.02
3.90	1.272	2°.520	1°.99
4.03	0.567	1°.058	1°.87
7.88	1.902	4°.137	2°.17
8.05	1.122	2°.301	2°.05
8.22	0.454	0°.900	1°.98
7.89	0.136	0°.257	1°.88

A comparison of the lowerings in water and in aqueous hydrogen dioxide will show that the latter are somewhat greater than the former, and are, therefore, analogous to the results obtained with sulphuric acid.

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[1] This JOURNAL, 27, 433 (1902).

While the lowering of the freezing-point of aqueous hydrogen dioxide produced by salts and bases is less than the lowering of the freezing-point of water produced by the same concentrations of the same substances, the lowering of the freezing-point of aqueous hydrogen dioxide produced by acids is greater than the lowering of the freezing-point of water produced by these same substances. The explanation of the results obtained with salts and bases, already suggested,[1] seems to be quite satisfactory. These compounds in solution unite with the hydrogen dioxide, forming complex, unstable substances. This conclusion, as has already been pointed out, is in accord with the recent work of Tanatar.[2]

The acids seem to be more strongly dissociated by hydrogen dioxide than by water, and, consequently, produce a greater lowering of the freezing-point of the former solvent. This conclusion is in accord with the work of Calvert,[3] who showed that the dielectric constant of hydrogen dioxide is probably higher than that of water.

CHEMICAL LABORATORY,
JOHNS HOPKINS UNIV.,
June, 1903.

THE ACTION OF ACETYL CHLORIDE ON SELENIC ACID.

BY ARTHUR B. LAMB.

Several attempts have been made to secure selenium trioxide, *i. e.*, the anhydride of selenic acid. None of them have been distinctly successful, though for a number of reasons one would suppose that such a body might exist. The analogous oxide of sulphur, for instance, is decidedly stable. Again, the stability of selenium dioxide, considered in connection with the very generally increasing stability of acidic oxides with their increasing oxygen content, points in the same direction.[4]

[1] This JOURNAL, 28, 290 (1902).
[2] Ztschr. anorg. Chem., 28, 255.
[3] Ann. d. Phys., 1, 483.
[4] Michael and Conn: This JOURNAL, 23, 444.

Cameron and Maccallan[1] seem to have most nearly succeeded in securing this body. They digested selenic acid, which they for the first time had been able to obtain anhydrous, with phosphoric anhydride. A white, granular precipitate resulted, which some unpublished analyses roughly indicated to be selenium trioxide.

A repetition of this experiment by the writer gave a similar precipitate, but in too small amounts for a quantitative analysis. Qualitative tests, however, showed a partial reduction to selenious acid, which might indicate a partial dehydration, and subsequent evolution of oxygen.

Digestion of the acid with anhydrous perchloric acid was also tried. The perchloric acid was prepared according to the method given by Michael and Conn.[2] Both an anhydrous selenic acid and an acid containing a slight amount of water were employed. The digestions were continued from three to four hours at 100° and 140°. At the end, however, in every case the perchloric acid could be distilled off unchanged.

The action of pure, dry acetyl chloride was then tried, and, while the anhydride of selenic acid was not obtained, a reaction of some interest was brought to light.

The selenic acid used in this, as well as in the previous experiments, was prepared in successive steps from pure selenium according to methods described by Thomsen,[3] and by Cameron and Maccallan. The resulting acid melted at 57°. The true melting-point of the acid as given by Cameron and Maccallan is 58°, and as very slight amounts of water greatly lower the melting-point, the acid as prepared was evidently nearly anhydrous. It contained, however, a trace of selenious acid, as shown by the faint coloration of its aqueous solution on the passage through it of hydrogen sulphide gas.

To the selenic acid, immersed in a bath of ice-water, the acetyl chloride, cooled to 0°, was added. A very energetic reaction ensued, with the immediate precipitation of a white, granular substance and the evolution of much gas. The white precipitate at first redissolved, but on the addition of more acetyl chloride became permanent and copious. It was found to be very hygroscopic, fuming strongly of hydrochloric acid when exposed to the air, and rapidly liquefying. Indeed the sulphuric acid in a desiccator must be very strong, else the substance will deliquesce even there. Qualitative tests by means of barium chloride and hydrochloric acid showed the complete reduction of the selenic acid to the selenious condition. Chlorine was also shown to be present in considerable amount.

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[1] Proc. Roy. Soc. (London), **46**, 13; Chem. News, **59**, 269.

[2] This JOURNAL, **23**, 444.

[3] Ber. d. chem. Ges., **2**, 598.

Samples of the precipitate were prepared for analysis by drying in a vacuum over strong sulphuric acid. The selenium was determined by the precipitation of the free element with sulphur dioxide and weighing on tared filters. The chlorine was determined as silver chloride.

I. 0.1872 gram substance gave 0.0743 gram Se.
II. 0.2431 gram substance gave 0.0921 gram Se.
III. 0.2021 gram substance gave 0.5116 gram AgCl.
IV. 0.1702 gram substance gave 0.4247 gram AgCl.

	Calculated for $SeCl_4$.	Found.			
		I.	II.	III.	IV.
Se	35.81	39.7	37.9	...	...
Cl	64.19	...	...	62.6	61.7

The physical properties, qualitative tests, and the analytical results, all indicate that the substance in question is selenium tetrachloride. The high values obtained in the analysis for selenium and the low ones for chlorine would be expected, both from the ease with which the tetrachloride absorbs water, with the loss of hydrochloric acid, and from the possible formation of a lower chloride of selenium. To eliminate this latter possible source of error, the precipitate was washed in some carefully dried carbon bisulphide, in which Ramsay and Evans[1] had found the lower chloride to be soluble, while the tetrachloride was insoluble. It was then analyzed by the much more satisfactory volumetric method of Fay and Norris.[2]

V. 0.2411 gram required the equivalent of 0.0856 gram Se or 35.5 per cent.

This result is in satisfactory agreement with the calculated percentage composition of selenium tetrachloride, when the possible errors of the analysis are considered.

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[1] J. Chem. Soc., **45**, 65.

[2] This JOURNAL, **18**, 703.

The reaction is practically a complete one, all the selenium being precipitated as tetrachloride. Nor does its vigor perceptibly decrease when the temperature is lowered to —20°. In spite too, of the fact that only infinitesimal amounts of water can be present as such, in either of the reagents, the reaction is apparently instantaneous.

Rose[1] discovered, long ago, that selenium tetrachloride is formed when selenates are heated with sodium chloride and sulphuric acid, chlorine being evolved, a reaction which is evidently somewhat analogous to the one here studied.

Cameron and Maccallan[2] also state that phosphorus pentachloride reacts violently with anhydrous selenic acid. It would not be surprising if selenium tetrachloride had also been formed here.

It is hoped to follow the course of the reaction between acetyl chloride and selenic acid more precisely, and to test its generality by substituting other halogens, especially fluorine, for chlorine.

The author wishes to thank Prof. A. Michael for his suggestion of, and assistance in, this research.

Contribution from the Kent Chemical Laboratory of the University of Chicago.

ESTERS OF SULPHURIC ACID AND OF CHLORSULPHONIC ACID.

By F. W. Bushong.

The secondary or neutral esters of sulphuric acid possess, as Nef[3] has shown, very low dissociation points. This explains the fact that it is impossible to obtain many of the homologous esters by the usual double decomposition method —interaction of dry silver sulphate with alkyl halides. Up to the present time only the methyl, ethyl, normal propyl, and isoamyl esters have been isolated. They have been found to act as alkylating agents.

[1] Pogg. Ann., 27, 575.
[2] Chem. News, 59, 233.
[3] Ann. Chem. (Liebig), 318, 40-50.

A further study of these and analogous compounds seems desirable, and the only possible method which presents itself for their synthesis at low temperatures is the interaction of sulphuryl chloride, Cl_2SO_2, or of chlorsulphonic esters, $Cl—SO_2—OR$, with the various free alcohols or their salts. The literature on this subject is rather conflicting and I have, therefore, taken up a careful study of these reactions, at the suggestion and under the guidance of Dr. Nef. My experiments are to be considered as preliminary, and it is the intention of Dr. Nef to continue further investigations in this direction.

Chlorsulphonic Ethyl Ester, $Cl—SO_2—OC_2H_5$.—This substance was first obtained, together with two others of the same empirical composition, by the union of sulphur trioxide with ethyl chloride.[1] Purgold proved it to be identical in its properties with the compound obtained in the interaction of potassium ethylsulphate and phosphorus pentachloride. Müller obtained the same compound, together with isethionic acid, by the addition of chlorsulphonic acid to ethylene.[2] It was also obtained by Sandmeyer[3] by the addition of ethyl hypochlorite to sulphur dioxide :

$$C_2H_5O—Cl + SO_2 \rightarrow Cl—SO_2—OC_2H_5.$$

Nef[4] has observed that chlorsulphonic ethyl ester is formed almost quantitatively by the interaction of free ethylsulphuric acid, which is now very easily accessible through Claesson's method,[5] and phosphorus pentachloride, the product being fractionally distilled under reduced pressure. This seemed, at first, the most practical method for isolating the compound under discussion. I have repeated Nef's experiments and analyzed the product obtained. It usually contains traces of oxychloride of phosphorus, which is removed by washing the oil repeatedly with water and subsequently drying it with calcium chloride and then again distilling under reduced pressure.

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[1] J. Chem. Soc., **10**, 100 (1857) ; Ann. Chem. (Liebig), **149**, 124 (1869) ; Ber. d. chem. Ges., **6**, 502 (1873).

[2] Ber. d. chem. Ges., **6**, 227 (1873).

[3] *Ibid.*, **19**, 860 (1886).

[4] Ann. Chem. (Liebig), **318**, 40 (1901).

[5] J. prakt. Chem., [2], **19**, 231 (1879).

I. 0.2257 gram substance gave, by the Carius method, 0.3695 gram $BaSO_4$.

II. 0.2666 gram substance required, after heating with lime, 19.24 cc. $AgNO_3$ solution (1 cc. = 0.00348 gram Cl) to precipitate AgCl, or gave 0.0669 gram Cl.

III. 0.2909 gram substance required 21.02 cc. $AgNO_3$ solution, or gave 0.0731 gram Cl.

	Calculated for $Cl—SO_2—OC_2H_5$.	Found. I.	II.	III.
S	22.18	22.48	....	....
Cl	24.52	....	25.09	25.14

Finally Behrend[1] prepared ethyl chlorsulphonate by the interaction of sulphuryl chloride and alcohol, according to the equation

$$Cl_2SO_2 + HOC_2H_5 \rightarrow HCl + Cl—SO_2—OC_2H_5.$$

Although Claesson[2] has shown that Behrend's work, in so far as it relates to the neutral esters of sulphuric acid, is unreliable, I have found that the following modification of Behrend's method yields ethyl chlorsulphonate to the extent of 60 per cent of the theoretical amount, and that the product is identical in its properties with that obtained by me from free ethylsulphuric acid and phosphorus pentachloride.

Sulphuryl chloride is brought into a distilling-flask, fitted with a doubly perforated stopper, through which are inserted the stem of a dropping-funnel and a glass tube drawn out to a capillary and extending below the surface of the acid chloride. The delivery-stem of the distilling-flask is connected with a wash-bottle containing water and then with an aspirator, and thus a steady stream of air, well dried with calcium chloride, is drawn through the apparatus. The distilling-flask is now immersed in a freezing-mixture of ice and salt, and absolute alcohol (a little in excess of 1 molecule) added drop by drop from the separatory-funnel. When all the alcohol has been added the freezing-mixture is removed, but the air current kept up for half an hour, or until the solution acquires the room temperature and becomes perfectly colorless. The reaction-products now appear in two layers, which are separated. The lower one consists mainly of ethyl chlorsulphonate, and, after washing with cold water, drying with calcium chloride, and distilling once under reduced pressure, is practically pure. The upper layer, on distillation under reduced pressure, gives off much hydrochloric acid and yields only small amounts of diethyl sulphate and of ethyl chlorsulphonate. There is much charring.

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[1] J. prakt. Chem. [2], **15**, 28 (1877).

[2] *Loc. cit.*

The analysis of the product thus obtained (b. p. 52° under 14 mm. pressure) gave the following figures:

I. 0.3372 gram substance gave, by the Carius method, 0.5528 gram $BaSO_4$.

II. 0.4108 gram substance required, after heating with lime, 28.20 cc. $AgNO_3$ solution (1 cc. = 0.00349 gram Cl), or gave 0.0984 gram Cl.

III. 0.3450 gram substance required 23.53 cc. $AgNO_3$ solution, or gave 0.0821 gram Cl.

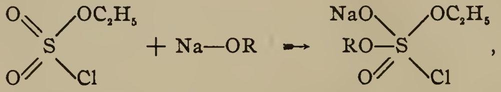
	Calculated for $Cl—SO_2—OC_2H_5$.	Found.		
		I.	II.	III.
S	22.18	22.51	....	....
Cl	24.52	....	23.96	23.80

Ethyl chlorsulphonate, made by either of the methods just described, is a colorless, limpid liquid possessing a pungent odor and which irritates the eyes and excites tears. It boils at 52° under 14 mm. and at 58° under 20 mm. pressure. Its specific gravity was found to be 1.263 at 18° (Westphal). The substance is soluble in ligroin, chloroform, and ether, but attacks ether when warmed. It dissolves in fuming nitric acid and is precipitated unchanged by addition of water. Water affects it only slightly, even after standing with it for weeks in the cold. On heating, however, decomposition quickly sets in. Thus, 4.8 grams of the ester, heated in a distilling-flask containing 40 cc. of water (temperature of bath 125° to 130°), gave 130 cc. ethyl chloride or 16 per cent of the theoretical amount.

Claesson[1] has shown that ethyl chlorsulphonate is decomposed with violence in the cold by ethyl alcohol, giving varying quantities of ethyl ether, ethyl chloride, hydrogen chloride, ethylsulphuric acid, and diethyl sulphate (never over 20 per cent), and I have confirmed these observations.

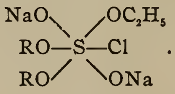
I. The Action of Chlorsulphonic Ethyl Ester on Sodium Alcoholates.

Sodium alcoholates (1.5 to 2 molecules), in ligroin or ethereal suspension, react with violence on the addition of ethyl chlorsulphonate. When absolute ether and only 1.5 molecules of the alcoholate are used, an almost clear solution results after some standing. This indicates the formation of an addition-product,



I.

and possibly also some ortho product,



II.

From the addition-product I., one would expect by subsequent loss of NaCl, the quantitative formation of a mixed ester of sulphuric acid, RO—SO_2—OC_2H_5. The facts are, however, as follows. There are always five reaction-products in varying proportions:

I. Alkyl ethylsulphate, RO—SO_2—OC_2H_5; the yield varies according as R is C_2H_5, C_5H_{11}, C_4H_9, or C_3H_7 from 37 to 62.2 per cent of the theory.

II. Alkyl sodium sulphate, RO—SO_2—ONa; 26 to 47.6 per cent according as R is C_2H_5, C_3H_7, C_4H_9, or C_5H_{11}.

III. A mixed ether, ROC_2H_5; determined as 27.7 per cent in one case only ($NaOC_2H_5$).

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[1] J. prakt. Chem. [2], 19, 231 (1879).

IV. Sodium sulphate; found to vary from 5 to 11 and 21.8 per cent, as the alcoholate used consisted of ethylate, isobutylate, or isoamylate.

V. Alcohol, ROH; not determined quantitatively and probably due to excess of alcoholate used.

From this it is evident that the reactions are very complicated, as is also the case when free ethyl alcohol acts on ethyl chlorsulphonate (see above). The formation of the mixed ether (III.) and of sodium alkyl sulphate (II.) cannot possibly be ascribed to the further action of the alcoholate on the neutral sulphate (I.) first formed,

$$\mathrm{RO{-}SO_2{-}OC_2H_5 + NaOR \longrightarrow ROC_2H_5 + RO{-}SO_2{-}ONa},$$

as was proved by a special experiment using the ethylate and ethylsulphate, no action taking place at ordinary temperature after three hours standing in ligroin suspension. A complete explanation of these results cannot at this time be presented, as further experiments are necessary to decide between equally plausible theories. Suffice it to say at this point that various experiments show that ethyl chlorsulphonate (*e. g.*, behavior towards amines) is an energetic alkylating agent, which points to a ready dissociation of this compound into ethylidene[1] and chlorsulphonic acid,

$$\genfrac{}{}{0pt}{}{\nwarrow}{\swarrow}\mathrm{CH{-}CH_3 + Cl{-}SO_2{-}OH}.$$

On this basis, for instance, the ether formation (III.) and formation of sodium alkyl sulphate (II.), as well as of sodium sulphate (IV.), can easily be understood.

Chlorsulphonic Ethyl Ester and Sodium Ethylate.—Twenty-five grams (2 mols.) freshly prepared sodium ethylate, dried at 180° in a hydrogen stream at reduced pressure, were suspended in 100 grams purified gasoline (b. p. 110° to 125°) and 25 grams ethyl chlorsulphonate slowly added by means of a dropping-funnel, during which operation the mixture was continually agitated and cooled by means of a freezing-mixture of ice and salt. The temperature of the solution was then allowed to rise to about 10° and kept there until the odor of the acid ester had disappeared. The gasoline filtrate gave, after distillation by means of a Glinsky apparatus, 2.85 grams of ethyl ether, or 27.7 per cent of the theory. It has been proved by a special experiment that ether (3.62 grams) and gasoline (100 cc.) can very well be separated by fractional distillation (3.56 grams being recovered). The amount of diethyl sulphate, distilling between 96° at 18 mm. and 96° at 14 mm., obtained from the gasoline by fractional distillation under reduced pressure, was 9.92 grams, or 37.2 per cent of the theory. The salt residue, insoluble in gasoline, was now examined. It was dissolved in water and the solution then saturated with carbon dioxide and evaporated to dryness under reduced pressure. Digestion with absolute alcohol yielded 12.2 grams of sodium ethylsulphate, 47.6 per cent of the theory. The residue insoluble in alcohol gave, on dissolving in water, acidifying with hydrogen chloride, etc., 2.05 grams of barium sulphate, which corresponds to 1.25 grams of sodium sulphate, 5 per cent of the theory.

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[1] Ann. Chem. (Liebig), 318, 1–57 (1901).

Ethyl Isoamyl Sulphate, $C_2H_5O—SO_2—OC_5H_{11}$.—Twenty-two grams (1.5 mols.) sodium isoamylate, dried at 220° in a hydrogen atmosphere at reduced pressure, were suspended in 100 cc. absolute ether and cooled in a freezing-mixture of ice and salt, and 19.5 grams ethyl chlorsulphonate added, drop by drop. The temperature of the reaction-mixture was now allowed to rise spontaneously to about 15°. It was observed that the sodium isoamylate gradually dissolved and that no salt separation took place after half an hour's standing at room temperature. On heating the mixture under a reversed condenser, much salt deposition took place. The ethereal filtrate was first distilled at about 100 to 150 mm. pressure in order to remove the excess of ether, and the amyl alcohol and amyl ethyl ether (a fair amount is present, but it was found impossible to separate it quantitatively from the amyl alcohol) formed in the experiment.

The residual oil was now distilled at about 18 mm. pressure. There was much charring and evolution of sulphur dioxide, but the distillate, after washing with dilute sodium hydrate and drying with calcium chloride, yielded 5 grams, or 37 per cent of the theoretical amount, of pure ethyl isoamyl sulphate (see below). The salt residue, insoluble in ether, was worked up as in the ethyl series—*i. e.*, dissolved in water, saturated with carbon dioxide, etc. Absolute alcohol extracted 7.4 grams of sodium isoamyl sulphate,[1] or 29 per cent of the theory. The insoluble salt residue yielded 6.88 grams of barium sulphate, corresponding to 4.19 grams or 21.8 per cent sodium sulphate.

In a second experiment 34 grams of sodium isoamylate, 150 cc. ether, and 30 grams ethyl chlorsulphonate were used. The ethereal solution was not, however, heated under the reversed condenser. On adding about 25 grams of water a thick, gelatinous mass of salts was precipitated, which dissolved on addition of more water (125 cc.). The ethereal and aqueous solutions were now worked up as before. The oil that remained after the removal of the amyl alcohol and amyl ethyl ether was, however, not directly distilled, but first again taken up in ether, washed with dilute caustic alkali, dried with calcium chloride, and then distilled at reduced pressure. Thus 20 grams, or 49 per cent, of pure ethyl isoamyl sulphate were obtained.

0.4636 gram substance gave, by the Carius method, 0.5646 gram $BaSO_4$.

	Calculated for $C_2H_5O—SO_2—OC_5H_{11}$.	Found.
S	16.34	16.72

Ethyl isoamyl sulphate is a colorless oil resembling diethyl sulphate. Its odor is less agreeable, however, and reminds one of that of bananas. It boils at 127° to 128° under 15 mm. pressure, and possesses the sp. gr. 1.079 at 20° (Westphal). It is insoluble in, and not affected by, cold water, is readily soluble in alcohol, ether, and ligroin. Heated to 140° it begins to decompose rapidly.

Ethyl Isobutyl Sulphate, $C_2H_5O—SO_2—OC_4H_9$.—Proceeding in a manner exactly like that described in the last experiment, of the amyl series, 25 grams (1.5 mols.) sodium isobutylate, suspended in 100 cc. absolute ether, were treated with 30 grams of ethyl chlorsulphonate. The following reaction-products were isolated:

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[1] It is assumed here, but not certain, that this salt is pure and free from sodium ethylsulphate. The same remark holds good of the corresponding salts obtained in the isopropyl and isobutyl series.

Ethyl isobutyl sulphate, 18.7 grams, or 50 per cent of the theory; sodium isobutyl sulphate, 9.6 grams, or 26 per cent of the theory; sodium sulphate, 3.2 grams, or 11 per cent of the theory.

The ethyl isobutyl sulphate obtained boils at 108° under a pressure of 13 mm. and possesses the sp. gr. 1.098 at 23° (Westphal). It is a colorless oil, insoluble in water, with an odor similar to that of mandrake.

0.6276 gram substance gave, by the Carius method, 0.8183 gram $BaSO_4$.

	Calculated for $C_2H_5O—SO_2—OC_4H_9$.	Found.
S	17.60	17.90

Ethyl Isopropyl Sulphate, $C_2H_5O—SO_2—OC_3H_7$.—The following results were obtained on treating 27 grams (2 mols.) sodium isopropylate, suspended in about 100 cc. ether, with 22.8 grams ethyl chlorsulphonate: Crude ethyl isopropyl sulphate, 16.2 grams, or 62.2 per cent; sodium isopropyl sulphate, 7.5 grams or 29.3 per cent of the theory. The ethyl isopropyl sulphate is much less stable than the other sulphates described, and consequently there is much loss in attempting to distil it even at reduced pressure. Its boiling-point is 105° at 18 mm. pressure, and the specific gravity at 21° was found to be 1.143 (Westphal). For the analysis, a distilled portion was taken up in ether, washed with dilute caustic soda, dried with calcium chloride, and then the ether removed by heating in a vacuum to 60°.

0.4904 gram substance gave, by the Carius method, 0.6664 gram $BaSO_4$.

	Calculated for $C_2H_5O—SO_2—OC_3H_7$.	Found.
S	18.95	18.65

The sodium isopropyl sulphate obtained closely resembles sodium isobutylsulphate in appearance, soapy feel, and solubility in water and alcohol. A portion of it was hydrolyzed by means of hydrochloric acid and the alcohol thus obtained found to boil between 79°.5 to 82°. It gave acetone by oxidation as was proved by its conversion into indigo by condensation with *o*-nitrobenzaldehyde.

II. The Action of Sulphuryl Chloride on Sodium Alcoholates.

Since sulphuryl chloride and ethyl alcohol give over 60 per cent of the theoretical yield of ethyl chlorsulphonate, it is to be expected that sulphuryl chloride and sodium alcoholates (two or more molecules) will give results entirely analogous to those obtained above in the interaction of ethyl chlorsulphonate with sodium alcoholates, since alkyl chlorsulphonates must first be formed as intermediate products. This was found to be the case. There is, however, always in addition a formation of sulphite which, in the case of sodium isopropylate, amounted to 48.6 per cent of the theory. This can only be understood on the assumption that the dissociation-products[1] of sulphuryl chloride, *i. e.*, sulphur dioxide and chlorine, and not this reagent as such, act on the alcoholates.

Sulphuryl Chloride and Sodium Ethylate.—Thirty grams (3 mols.) of sodium ethylate, suspended in 100 grams of ligroin (b. p. 62° to 67°), were treated with 20 grams of sulphuryl chloride, proceeding in a manner entirely analogous to that described in the case of the ethyl chlorsulphonate. The odor of ethyl chlorsulphonate is at first very marked, and does not entirely disappear until the temperature reaches 15°. The ligroin filtrate yielded 6.5 grams, or 29.5 per cent of diethyl sulphate (b. p. 96° to 98°) at 15 mm. pressure. The salt residue was found to contain 11.8 grams, or 54 per cent, of sodium ethylsulphate (by extraction with alcohol after treatment in aqueous solution with carbon dioxide, etc.). It was also found to contain 0.73 gram of sodium sulphate (4.9 per cent) and 0.067 gram (or 0.7 per cent) sulphur dioxide, as determined by titration with N/10 iodine solution.

Diisoamyl Sulphate from Sulphuryl Chloride and Sodium Isoamylate.—Fifty-two grams (3.2 mols.) sodium isoamylate,

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[1] Nef: Ann. Chem. (Liebig), 318, 40 (1901).

150 cc. absolute ether, and 20 grams of sulphuryl chloride gave 8 grams, or 23 per cent of diisoamyl sulphate,[1] b. p. 149° to 151° at 12 mm. pressure. The other products formed were not isolated.

Diisobutyl Sulphate, $(C_4H_9O)_2SO_2$. — Seventy grams of sodium isobutylate (3.25 mols.), suspended in absolute ether and treated with 30 grams of sulphuryl chloride, etc., gave 27.5 grams, or 55 per cent, of diisobutyl sulphate, b. p. 133° to 134° under 19 mm. pressure. For analysis the distillate was taken up in ether, washed with dilute caustic soda, dried with calcium chloride, and then the last traces of ether removed by heating in a distilling-flask from 60° to 80° at reduced pressure.

0.4308 gram substance gave, by the Carius method, 0.4848 gram $BaSO_4$.

	Calculated for $(C_4H_9O)_2SO_2$.	Found.
S	15.25	15.45

Diisobutyl sulphate cannot be prepared by the interaction of silver sulphate and isobutyl iodide.[2] As prepared above, its refractive index for sodium light was found to be 1.415, and the specific gravity is 1.042 at 23° (Westphal). The salt residue in the experiment described above was found to contain much sulphite (not determined quantitatively), and also yielded 6.6 grams, or 18 per cent, of sodium isobutyl sulphate, on digestion with alcohol.

Diisopropyl Sulphate, $(C_3H_7O)_2SO_2$.—Thirty-one grams (3.5 mols.) of sodium isopropylate, ether, and 15 grams of sulphuryl chloride gave 4.5 grams of crude diisopropyl sulphate, heated to 60° at reduced pressure, in a distilling-flask. The substance is very unstable,[3] undergoing decomposition on standing at ordinary temperature. On attempting to distil it at 18 mm. pressure, a small portion passed over at about 106°. For analysis the crude oil, not distilled, was taken up in ether, washed with caustic alkali, dried with calcium chloride, and the ether removed by heating to 60° at reduced pressure. The substance evidently was not quite pure.

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[1] Nef: *Ibid.*, **318**, 42 (1901).

[2] Ann. Chem. (Liebig), **318**, 43 (1901).

[3] Berthelot has recently obtained this substance from propylene and sulphuric acid.

0.3454 gram substance gave, by the Carius method, 0.3956 gram $BaSO_4$.

	Calculated for $(C_3H_7O)_2SO_2$.	Found.
S	17.60	15.73

The salt residue in the experiment just described gave 18 grams, or 22 per cent, of sodium isopropyl sulphate on digestion with alcohol. The salt left, insoluble in alcohol, was found to contain 3.456 grams of sulphur dioxide (or 48.6 per cent) by titration with N/10 iodine solution.

III. The Action of Ethyl Chlorsulphonate upon Aniline.

This reaction has already been studied by Wenghöffer,[1] who obtained free sulphanilic acid as the only reaction-product. It is evident from the experiments of Wagner[2] and of W. Traube[3] and Bamberger[4] that phenylsulphaminic acid must first have been formed, which readily goes over into sulphanilic acid. It is noteworthy that no trace of an ester is formed according to the equation

$$\begin{aligned} &C_6H_5NH_2 + Cl{-}SO_2OC_2H_5 \longrightarrow \\ &\qquad C_6H_5NH{-}SO_2OC_2H_5 + HCl \longrightarrow \\ &\qquad\qquad H_2NC_6H_4{-}SO_2OC_2H_5 + HCl, \end{aligned}$$

as was proved by special experiments. Preliminary experiments with ethyl chlorsulphonate (1 mol.) and aniline (3 mols.) in ligroin solution have proved, furthermore, that much ethylaniline (in a free state as well as in form of the sulphate) is formed in this reaction, as was established by its conversion into ethylphenylnitrosamine.

These experiments, as well as the isolation of a mixed ether, ROC_2H_5, in the interaction of ethyl chlorsulphonate with free alcohols and their salts, show that ethyl chlorsulphonate is an alkylating agent, acting just as ethyl halides, nitrate, sulphate, etc.[5]

[1] J. prakt. Chem. [2], **31**, 1803.

[2] Ber. d. chem. Ges., **19**, 1157.

[3] *Ibid.*, **23**, 1653.

[4] *Ibid.*, **30**, 2275.

[5] Nef: Ann. Chem. (Liebig), **309**, 126–189; **318**, 1–40, 138–147.

I wish to cordially thank Dr. Nef for his careful guidance and cheerful help as well as for personal kindness shown during the prosecution of this work.

Contribution from the Kent Chemical Laboratory of the University of Chicago.

THE ACTION OF CARBON MONOXIDE ON SODIUM ALCOHOLATES ALONE AND IN THE PRESENCE OF SALTS OF FATTY ACIDS.

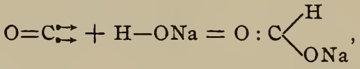
By W. A. Beatty.

The synthesis of salts of fatty acids by the action of carbon monoxide on sodium alcoholates gives exceedingly poor yields and has been applied by Geuther and Fröhlich[1] with success only in two cases, namely, sodium methylate and ethylate.

The experiments of Nef[2] establish decisively that these syntheses take place in two stages: 1. The carbon monoxide absorbs the sodium hydroxide resulting from the dissociated sodium alcoholate molecules,

$$C_nH_{2n} + HONa \rightleftarrows C_nH_{2n+1}ONa,$$

and thus sodium formate,



$$O{=}C\rightleftarrows + H{-}ONa = O:C\begin{matrix}\diagup H \\ \diagdown ONa\end{matrix},$$

is first formed. 2. The sodium formate is subsequently, and only to a very limited extent, absorbed by the alkylidene molecules simultaneously set free, as follows:

$$C_nH_{2n}\rightleftarrows + H{-}COONa = C_nH_{2n+1}COONa.$$

It is also clear from the experiments of Nef that the formation of alkylated fatty acids, which was observed by Geuther and his students on passing carbon monoxide over a mixture of a sodium alcoholate and a salt of a fatty acid, is an alkylation phenomenon.[3] The carbon monoxide unites with the sodium hydroxide coming from the dissociated sodium alcoholate molecules to give sodium formate; the alkylidene molecules, liberated at the same time, then simply alkylate the fatty acid present,[1] *e. g.*:

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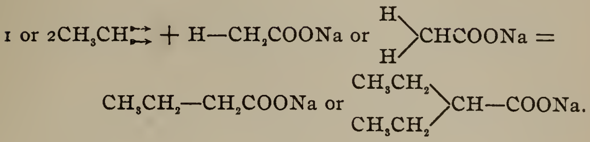
[1] Ann. Chem. (Liebig), **202**, 288–331.

[2] *Ibid.*, **318**, 185.

[3] *Ibid.*, **310**, 316–335; **318**, 143–172. Cf. *Ibid.*, **202**, 288–331; **218**, 57.



$$1 \text{ or } 2CH_3CH\rightrightarrows + H{-}CH_2COONa \text{ or } \begin{matrix}H\\H\end{matrix}\!>CHCOONa =$$

$$CH_3CH_2{-}CH_2COONa \text{ or } \begin{matrix}CH_3CH_2\\CH_3CH_2\end{matrix}\!>CH{-}COONa.$$

It seemed desirable, in view of the new interpretation of these syntheses, to repeat some of the experiments of Geuther and his students. I have therefore undertaken this work at the suggestion and under the direction of Dr. J. U. Nef.

The Action of Carbon Monoxide on Sodium Isoamylate.

This reaction has been studied by Geuther and Fröhlich,[2] who obtained much formic acid, some valeric acid, and an unsaturated acid, $C_{10}H_{18}O_2$, but no trace of isoamylformic acid. Geuther and his students used carbon monoxide made from yellow prussiate of potash and concentrated sulphuric acid, and there is some doubt whether every trace of air was excluded in their experiments. In fact it was sometimes found impossible to repeat or confirm their work. I shall, therefore, simply describe my own results and the exact conditions under which they were obtained, indicating and explaining briefly, wherever possible, the points not in accord with previous observations.

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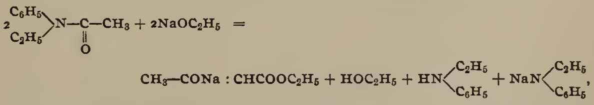
[1] Experiments carried out by Mr. Higley under my direction have now made it highly probable that at least some of these reactions proceed through an intermediate formation of acetoacetic ether. Thus ethylacetanilide (2 mols.) and sodium ethylate give, by aldol condensation (Ann. Chem. (Liebig), **298**, 319),



$$2\begin{matrix}C_6H_5\\C_2H_5\end{matrix}\!>N{-}\underset{\underset{O}{\|}}{C}{-}CH_3 + 2NaOC_2H_5 =$$

$$CH_3{-}CONa : CHCOOC_2H_5 + HOC_2H_5 + HN\!<\!\begin{matrix}C_2H_5\\C_6H_5\end{matrix} + NaN\!<\!\begin{matrix}C_2H_5\\C_6H_5\end{matrix},$$

acetoacetic ether, which is thereupon converted, in part, into mono- and diethylated acetoacetic ether by the ethylidene molecules present. These substances then undergo the "acid splitting," and thus give rise to the mono- and dialkylated acetic acids obtained by Nef and by Geuther in their syntheses. Mr. Higley will soon publish his results in detail. J. U. NEF.

[2] Ann. Chem. (Liebig), **202**, 294.

The reaction-products obtained by me in the experiment under discussion were, besides valeric acid, 1, isopropylisoamylacetic acid; 2, decyl alcohol or isopropylisoamylethyl alcohol; 3, a lactone, $C_{11}H_{20}O_2$, or 1-isobutyl-2-isopropylbutyrolactone. As these substances had all been isolated and carefully studied by Nef in his experiments with sodium isoamylate my work was much simplified. It consisted in establishing rigidly the identity of the products obtained by me with the corresponding ones obtained by Nef. Furthermore, some time was spent in the study of an oxidation-product obtained from the lactone, $C_{11}H_{20}O_2$. A dibasic acid, α- or *trans*-isopropylisobutylsuccinic acid was thus obtained. This is isomeric—not identical—with a β- or *cis*-isopropylisobutylsuccinic acid obtained in two ways by synthesis, and up to the present time I have not been successful in converting one of these isomers into the other.

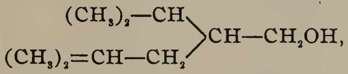
The carbon monoxide for all my experiments was prepared from oxalic acid and concentrated sulphuric acid. The carbon dioxide was removed from the gaseous mixture by means of washing-bottles containing concentrated caustic potash.

The carbon monoxide was collected in a gasometer and then purified and dried before use, as follows: It was first passed through two large Bunsen wash-bottles containing chromous chloride (to remove oxygen), and then through two tubes containing soda-lime and fused calcium chloride, and finally through a wash-bottle containing sulphuric acid.

The sodium isoamylate was prepared in the usual way, and the last traces of amyl alcohol were removed by heating in a bath at 220° under 20 to 30 mm. pressure. 450 grams of sodium isoamylate were heated in four large, glass tubes so placed in a sealed-tube furnace that the carbon monoxide had a continuous passage through the apparatus. The exit-tube was connected with an empty wash-bottle and then with a Schiff's azotometer. The rate of flow and absorption of gas could thus be roughly determined. Precautions were also taken to avoid an entrance of air when the furnace was turned off at night by closing the end of the apparatus with a clamp and allowing the gas to flow at full pressure into the cooling tubes.

The sodium isoamylate was heated (temp. 180° to 190°) in a carbon monoxide atmosphere for about two weeks, seven hours daily. At the end of this time the tube contents were colored brown and some liquid had collected at the ends of the tubes. The mass was poured into much water and a larger amount of oil separated on top of the strongly alkaline aqueous solution. The neutral oils were extracted by means of ether and then dried with potassium carbonate. On distillation at reduced pressure, 12.2 grams of oil boiling between 60° and 100° under 60 mm. pressure (chiefly amyl alcohol) and 101.4 grams of oil boiling between 100° and 190° at 16 mm. pressure were obtained, besides 33 grams of resin left in the distilling-flask. The main fraction (101.4 grams) was now treated with a solution of 101.4 grams of caustic potash in twice its weight of alcohol, and heated with a return-condenser for ten hours, in order to saponify esters of acids and convert the lactone, $C_{11}H_{20}O_2$, into the corresponding γ-oxyundecylenic acid. The greater part of the alcohol was then distilled off and the residue treated with much water and extracted with ether. The ethereal extract, dried with potassium carbonate, gave, on distillation, 8 grams of oil (b. p. 130° to 208°), chiefly amyl alcohol and 25 grams of decyl alcohol boiling between 209° and 212°. Fourteen and seven-tenths grams of oil, boiling between 212° and 270°, were also obtained.

The decyl alcohol obtained was found to be identical with a decyl alcohol first observed by Borodin[1] and later by Guerbet.[2] Its constitution as isopropylisoamylethyl alcohol,



$$\left.\begin{array}{r}(CH_3)_2\text{—}CH\\(CH_3)_2{=}CH\text{—}CH_2\end{array}\right> CH\text{—}CH_2OH,$$

has been determined by Nef.[3] The identity was proved by converting it by means of potash-lime into the corresponding isopropylisoamylacetic acid (b. p. 241°) and its well-crystallized derivatives, the amide (m. p. 112°), and anilide (m. p. 105°). These were found to agree in all their properties with the corresponding substances obtained by Nef.

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[1] Ber. d. chem. Ges., **5**, 480.

[2] Bull. soc. chim., **21**, 450.

[3] Ann. Chem. (Liebig), **318**, 151.

The alkaline solution resulting from the above-mentioned saponification yielded, on acidifying with diluted sulphuric acid and extracting with ether, a total of 31.6 grams of oily acids. On distillation at 9 mm. pressure, the following fractions were obtained: Six grams boiling between 90° and 125°; 5.7 grams between 125° and 130°; 12.7 grams between 135° and 137°; and 2 grams between 137° and 151°, leaving 5 grams of resin in the distilling-flask.

On redistillation and subsequent treatment of the higher boiling fractions with dilute soda, a small amount of oil was found to be neutral in character. It was therefore extracted by ether, and on fractionation yielded 4 grams of the γ-oxyundecylenic acid lactone, $C_{11}H_{20}O_2$ (b. p. 141° to 145° at 10 mm. pressure). The soda solutions gave, on working up for acids, 3 grams of isovaleric acid (b. p. 174° to 176°) and 10 grams of isopropylisoamylacetic acid (b. p. 135° to 137° at 9 mm. pressure). The latter was, in part, converted into the crystallized amide and anilide mentioned above, and thus sharply identified.

The original alkaline solution was now worked up by acidifying with dilute sulphuric acid and extracting with ether. After drying with calcium chloride and driving off the ether the residual oil was distilled. Fifty and seventh-tenths grams of oil boiling up to 125° at 40 mm. pressure (chiefly formic and isovaleric acid) and 71.4 grams of oil boiling between 125° to 200° at 15 mm. pressure, were obtained, and 32 grams of resin were left in the distilling-flask. On treatment of the higher boiling fraction with soda a fair amount of oil was found to be neutral. It was therefore extracted by ether and yielded 10 grams of pure lactone, $C_{11}H_{20}O_2$ (b. p. 142° to 144° at 11 mm.). The soda solutions gave, on working up for acids, besides much isovaleric acid, 15 grams of pure isopropylisoamylacetic acid (b. p. 241°).

The lactone, $C_{11}H_{20}O_2$, obtained in this experiment was identified by its conversion into the corresponding undecylenic acid and its crystalline amide[1] (m. p. 82°).

From the above it will be seen that 450 grams of sodium isoamylate yielded, after treatment with carbon monoxide for twelve days, 25 grams of decyl alcohol (isopropylisoamylethyl alcohol), 14 grams of γ-oxyundecylenic acid lactone, $C_{11}H_{20}O_2$, 25 grams of isopropylisoamylacetic acid, besides some amyl alcohol and much formic and isovaleric acids.

The substances obtained in this experiment were sharply identified by conversion into well-known crystalline derivatives. Their analysis was deemed unnecessary because the same reaction-products were obtained in an experiment whose description follows and in which all the substances obtained were analyzed.

The Action of Carbon Monoxide on a Mixture of Sodium Acetate and Sodium Isoamylate.

By passing carbon monoxide over an equimolecular mixture of sodium ethylate and sodium acetate at 160° to 200°, Geuther and Fröhlich[2] obtained, among other products, ethylacetic acid and diethylacetic acid. By using a mixture of sodium isoamylate and sodium acetate Poetsch[3] isolated large amounts of an acid, $C_7H_{14}O_2$, which, from its properties, must be considered as isoamylacetic acid. Nef obtained[4] from sodium isoamylate and ethylacetanilide, at 150°, a large yield of isoamylacetic acid. These results are due either to a direct alkylation of the sodium acetate or ethylacetanilide present, or to an alkylation of an acetoacetic acid derivative (formed as an intermediate product through aldol condensation) and subsequent "acid splitting" of the mono- and dialkylated acetoacetic acid derivative—as pointed out in a foot-note in the introduction. It is also obvious that the oenanthylic acid, $C_7H_{14}O_2$ (b. p. 222° to 226°), obtained by Loos[5] by the action of sodium ethylate on sodium isovalerate must be identical with ethylisopropylacetic acid.

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[1] Nef: Ann. Chem. (Liebig), **318**, 154–155.

[2] Ann. Chem. (Liebig), **202**, 288–331.

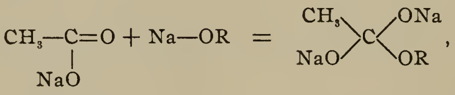
[3] *Ibid.*, **218**, 57.

[4] *Ibid.*, **318**, 145.

[5] *Ibid.*, **202**, 321.

Furthermore, Geuther and Fröhlich, as well as Poetsch, very frequently obtained in their experiments with sodium isoamylate neutral compounds which they regarded, without any further evidence, as ketones. It is obvious that one of these which was obtained by them in especially large amount and to which they give the boiling-point 203° to 210° was decyl alcohol, *i. e.*, the isopropylisoamylethyl alcohol mentioned above.

Finally, it is clear from what follows, that on mixing a sodium alcoholate with a sodium salt of a fatty acid (such as acetic or isovaleric acid) it is essential that the latter should be added, finely pulverized, directly to the alcoholic solution of the sodium alcoholate, and the alcohol subsequently removed by distillation in a hydrogen atmosphere at ordinary or reduced pressure. A more intimate mixture is thus obtained, and very probably a combination between the alcoholate and sodium salt of the fatty acid invariably takes place, *e. g.*,



and thus naturally an aldol condensation must take place by heat or on standing (even before the carbon monoxide is passed over the mixture). Such an addition-product was in fact isolated in the case of sodium ethylate and potassium acetate (see below).

Geuther and Fröhlich, as well as Loos and Poetsch, in the experiments alluded to, must have prepared their mixture of sodium alcoholate and sodium salt of a fatty acid in this way, for if one mixes intimately, in a mortar, dry sodium isoamylate and fused sodium acetate in equimolecular proportions, and then passes carbon monoxide over the mixture at 150° to 200°, the sodium acetate is left entirely unaffected. In this case the same reaction-products are obtained as when sodium isoamylate alone is used, as is evident from the following:

An equimolecular mixture, 310 grams, of sodium acetate and sodium isoamylate, obtained by grinding the two substances together in a mortar, was heated in the apparatus described above and carbon monoxide passed over it (temp. 180° to 200°) for eight days, seven hours daily. On working up as in the previous case—pouring into 4 liters of water, separating the neutral and acid components—the following products were obtained and sharply identified by conversion into well-defined and crystalline derivatives, and by analysis. The neutral portion gave, on the first fractionation, 25.7 grams of oil boiling from 70° to 90° at 60 mm., 14.5 grams boiling from 90° to 120° at 9 mm., and 18.9 grams oil boiling between 120° and 185° at 9 mm. pressure. Twenty-one grams of resin were left in the distilling-flask. The low-boiling oil was found to consist chiefly of isoamyl alcohol boiling from 129° to 131°. From the middle fraction, after two distillations, 9.1 grams of pure decyl alcohol boiling between 97° and 99° at 8 mm. pressure, were finally obtained. This was a fragrant oil that boiled at 210° to 212° and gave the following figures on analysis :

I. 0.2282 gram substance gave 0.6360 gram CO_2 and 0.2784 gram H_2O.

II. 0.1903 gram substance gave 0.5293 gram CO_2 and 0.2324 gram H_2O.

	Calculated for $C_{10}H_{22}O$.	Found. I.	II.
C	75.94	76.01	75.85
H	13.92	13.55	13.57

That the decyl alcohol obtained was isopropylisoamylethyl alcohol was proved by its conversion into isopropylisoamylacetic acid and its amide and anilide.

On refractionating the high-boiling neutral oil, 18.9 grams, two fractions were obtained and analyzed. The first of these boiled at 130° to 133° at 8 mm. and the second from 134° to 140° at the same pressure. No definite conclusion from the data obtained could be drawn concerning the nature of the product or products present.

It will be noticed that a similar product (14.7 grams, b. p. 212° to 270°) was obtained in the first experiment with sodium isoamylate and carbon monoxide alone (see above).

It is probable that some 1,3-decylglycol (α-isobutyl-β-isopropyltrimethyleneglycol),[1] as well as some amyl decylate and decylvalerate, were present, but I was unable to establish this rigidly by experiment. The high-boiling fractions were digested with alcoholic potash and thus 3 grams of decyl alcohol and 2 grams of a neutral oil (b. p. 132° to 136° at 10 mm. pressure), which gave no definite results on analysis, were obtained. The alkaline solution resulting from the saponification gave, on working up for acids, 3 grams of isovaleric acid (b. p. 174° to 176°) and 4.5 grams of oil boiling from 140° to 142° at 10 mm. pressure. The latter was found to be neutral towards soda and to consist chiefly of γ-oxyundecylenic acid lactone, $C_{11}H_{20}O_2$.

From the original alkaline solution, containing the acid reaction-products, 50 grams of crude, oily acids were isolated. On distillation, the following fractions were obtained: 9 grams boiling up to 60° at 60 mm. pressure; 8.9 grams boiling from 60° to 100° at 20 mm.; 20.6 grams boiling from 100° to 180° at 20 mm. pressure. Ten grams of resin remained in the distilling-flask. On treating the higher-boiling fraction with soda and extracting with ether, 10 grams of the lactone, $C_{11}H_{20}O_2$, boiling from 141° to 143° at 12 mm. pressure, were obtained.

I. 0.2120 gram substance gave 0.5566 gram CO_2 and 0.2028 gram H_2O.

II. 0.1176 gram substance gave 0.3091 gram CO_2 and 0.1139 gram H_2O.

	Calculated for $C_{11}H_{20}O_2$.	Found. I.	Found. II.
C	71.74	71.6	71.68
H	10.87	10.62	10.77

The lactone was also identified through conversion (4 grams) into the lime salt, which was crystallized from much water and dried at 100°.[2]

0.5108 gram salt gave 0.1578 gram $CaSO_4$.

	Calculated for $C_{22}H_{42}O_6Ca$.	Found.
Ca	9.05	9.08

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[1] Ann. Chem. (Liebig), **318**, 165.

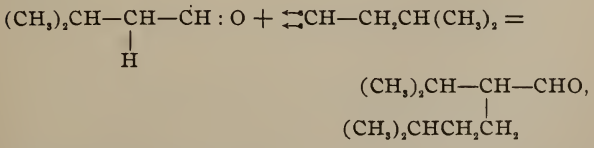
[2] Cf. Nef: *Loc. cit.*

The remainder of the lactone was converted into the corresponding undecylenic acid and its amide, m. p. 82°, and these were found to be identical in their properties with those given by Nef.

The soda solutions from which the lactone had been removed and the lower-boiling fractions, mentioned above, were found to contain chiefly two acids, much isovaleric acid (b. p. 175°), and about 15 grams of isopropylisoamylacetic acid (b. p. 241°), proved by conversion into the amide (m. p. 112°) and the anilide (m. p. 105°). The intermediate fraction, 2 grams only, may have contained traces of isoamylacetic acid, which boils at 212°, but it is certain that this substance is not an essential reaction-product in the experiment carried out as described above. Poetsch obtained, in a similar experiment from 746 grams of sodium isoamylate and 546 grams of sodium acetate, 40 grams of decyl alcohol (b. p. 203° to 206°), 50 grams of isovaleric acid (b. p. 165° to 200°), 80 grams of isoamylacetic acid (b. p. 200° to 240°, chiefly 212° to 213°), and 40 grams of acid boiling from 240° to 300° (isopropylisoamylacetic acid (?), lactone, $C_{11}H_{20}O_2$ (?)). The cause of the difference in the results obtained has already been discussed.

The formation of a primary decyl alcohol, its corresponding isopropylisoamylacetic acid, and a lactone, $C_{11}H_{20}O_2$, by the action of carbon monoxide on sodium isoamylate alone or in the presence of sodium acetate, as shown above, is easily understood in view of the experiments of Nef.[1]

Valeraldehyde, which is formed by the action of isoamylidene on sodium hydroxide, is alkylated by the excess of isoamylidene molecules present and thus isopropylisoamylacetaldehyde,



$$(CH_3)_2CH{-}\underset{\displaystyle H}{\underset{|}{CH}}{-}\dot{C}H:O + \leftrightarrows CH{-}CH_2CH(CH_3)_2 = (CH_3)_2CH{-}\underset{(CH_3)_2CHCH_2CH_2}{\underset{|}{CH}}{-}CHO,$$

is first formed, which is then in part reduced by the atomic hydrogen present to the corresponding decyl alcohol, and in part converted by the sodium hydroxide, according to the Dumas-Stas' reaction, into isopropylisoamylacetic acid.

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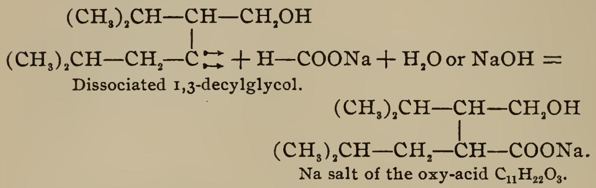
[1] Ann. Chem. (Liebig), 318, 147-173.

The valeraldehyde is also in part converted into the aldol which by reduction gives 1-isobutyl-2-isopropyltrimethyleneglycol. The 1,3-decylglycol,[1] or its monosodium salt thus formed, then reacts by alkylation with the sodium formate (resulting from the action of carbon monoxide on sodium hydroxide) to give the oxy-acid, $C_{11}H_{22}O_3$, which, on acidifying, goes over spontaneously into the lactone, $C_{11}H_{20}O_2$.



$$\begin{array}{l} (CH_3)_2CH{-}CH{-}CH_2OH \\ \qquad\qquad\qquad\quad | \\ (CH_3)_2CH{-}CH_2{-}C\rightleftarrows + H{-}COONa + H_2O \text{ or } NaOH = \end{array}$$

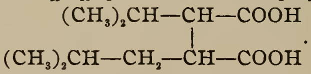
Dissociated 1,3-decylglycol.

$$\begin{array}{r} (CH_3)_2CH{-}CH{-}CH_2OH \\ | \qquad\quad \\ (CH_3)_2CH{-}CH_2{-}CH{-}COONa. \end{array}$$

Na salt of the oxy-acid $C_{11}H_{22}O_3$.

The interaction between carbon monoxide and sodium isoamylate is thus in every way analogous and comparable to that taking place between sodium isoamylate and formethylaniline which has been exhaustively investigated by Nef.

The Oxidation of the Lactone $C_{11}H_{20}O_2$ to α- or Trans-isopropylisobutylsuccinic Acid,



$$\begin{array}{r} (CH_3)_2CH{-}CH{-}COOH \\ | \qquad\quad \\ (CH_3)_2CH{-}CH_2{-}CH{-}COOH \end{array}.$$

The constitution of the lactone, $C_{11}H_{20}O_2$, as given above, follows from the fact that the corresponding oxy-acid, $C_{12}H_{22}O_3$, gives by oxidation with permanganate, or by treatment with potash-lime at 250°, a dicarboxylated acid, $C_9H_{18}{=}(COOH_2)$. This proves that the hydroxyl group in the oxy-acid must be present as a primary alcohol group, and consequently excludes another possible formula for the oxy-acid, *e. g.*:

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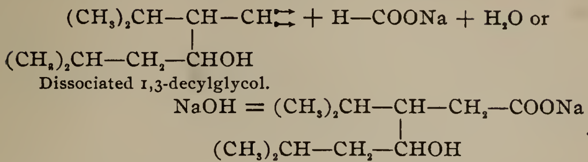
[1] Rosinger claims (Ann. Chem. (Liebig), **322**, 131-133) that the substance described by me (Ann. Chem. (Liebig), **318**, 165) was not 1,3-decylglycol but its monovalerate. This is incorrect, as my substance was heated for two hours with an excess of caustic potash at 110° and I obtained 39 grams of isovaleric acid from 201.4 grams valeraldehyde taken. Furthermore, I expressly state (p. 166) that my decylglycol was not affected by alcoholic potash. In his experiments, Rosinger has determined clearly the conditions under which the monovalerate of 1,3-decylglycol can be isolated as an intermediate product. J. U. NEF.



$$\begin{array}{l} \qquad (CH_3)_2CH—\underset{|}{CH}—CH\rightleftarrows + H—COONa + H_2O \text{ or} \\ (CH_3)_2CH—CH_2—CHOH \end{array}$$

Dissociated 1,3-decylglycol.

$$\begin{array}{l} NaOH = (CH_3)_2CH—\underset{|}{CH}—CH_2—COONa \\ \qquad (CH_3)_2CH—CH_2—CHOH \end{array}$$

Sodium salt of a γ-oxy-acid, $C_{11}H_{22}O_3$.

An oxy-acid of the constitution given here would be readily oxidized to a γ-ketonic acid or to a secondary amylisobutylketone but could not possibly give a dibasic acid, $C_{11}H_{20}O_4$, with the same number of carbon atoms—hence the constitution of the lactone, $C_{11}H_{20}O_2$, as given by Nef, must be correct.

Twenty grams of lactone, $C_{11}H_{20}O_2$, prepared according to Nef's method, were heated with a concentrated solution of caustic soda until the lactone had all dissolved. On cooling, a solution of 20 grams of potassium permanganate was added at once and the mixture (volume about 1 liter) allowed to stand in the cold until decolorized. After filtering, acidifying, extracting with ether, the oily reaction-product obtained was distilled at reduced pressure. Six grams of lactone, $C_{11}H_{20}O_2$, were recovered and the residue left in the distilling-flask (bath 200° at 9 mm.) solidified on cooling. It was washed with low-boiling ligroin and then crystallized from hot water, and thus about 12 grams of an acid, crystallizing in long needles and melting at 142°, were obtained.

0.2041 gram substance gave 0.4580 gram CO_2 and 0.1702 gram H_2O.

	Calculated for $C_{11}H_{20}O_4$.	Found.
C	61.10	61.19
H	9.26	9.26

A silver salt was made by adding a solution of the acid, carefully neutralized by means of dilute ammonia, to an excess of aqueous silver nitrate. The salt comes down as a white, flocculent precipitate, which was well washed and dried over sulphuric acid *in vacuo*.

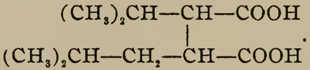
0.2218 gram salt gave, on ignition, 0.1110 gram Ag.

	Calculated for $C_{11}H_{18}O_4Ag_2$.	Found.
Ag	50.23	50.00

The *α*- or *trans*-isopropylisobutylsuccinic acid thus obtained is easily soluble in ether and alcohol, but almost insoluble in benzene and ligroin. A very small amount (0.1 gram) of a lower melting (109° to 115°) acid was found in the aqueous mother-liquors, but it was impossible to determine the nature of this product. It certainly is not isopropylsuccinic acid or the *β*- or *cis*-isopropylisobutylsuccinic acid obtained by synthesis (see below).

α- or *trans*-Isopropylisobutylsuccinic acid is also obtained in fine yield by heating the lactone $C_{11}H_{20}O_2$, with an excess of potash-lime at 250° until the evolution of hydrogen ceases. Thus, 6 grams of lactone gave 5 grams of oily-acid products from which 2.5 grams of the pure acid, melting at 142°, were obtained.

Synthesis of β- or cis-Isopropylisobutylsuccinic Acid,



$$\begin{array}{r}(CH_3)_2CH-CH-COOH\\ |\qquad\qquad\quad\\ (CH_3)_2CH-CH_2-CH-COOH\end{array}.$$

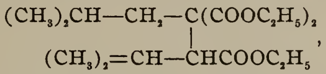
The symmetrical, dialkylated, succinic acids have usually been obtained by synthesis in two stereoisomeric, *cis*- and *trans*-, modifications which are mutually introconvertible by means of hydrogen chloride, acetic anhydride and acetyl chloride.

The *cis*-diisopropyl and the *cis*-diisobutylsuccinic acids have been isolated but up to the present time have not been converted into the corresponding *trans*-isomers. The terms *cis*- and *trans*- are simply relative terms to designate the two stereoisomers, the term *trans*- being applied to the higher melting and less soluble isomer.

It was, therefore, *a priori*, possible that a synthetic isopropylisobutylsuccinic acid would be obtained in the *cis* form only. This was found to be the case, and since this substance was found to be different from an isopropylisobutylsuccinic acid obtained from the lactone, $C_{11}H_{20}O_2$ (see above), it must be concluded that the latter is the *trans* modification. Up to the present time I have not been successful in converting these isomers into each other, although it must be admitted that neither of them has yet been exhaustively studied, and only one experiment was carried out in this direction. Heated in a sealed tube with concentrated hydrochloric acid at 200° to 230° the *cis*, as well as the *trans*, isomer was recovered unaltered.

The *cis*-isopropylisbutylsuccinic acid, which melts at 118° to 119°, was prepared, in two ways, synthetically :

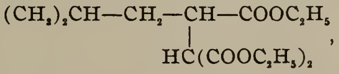
1. From sodium isobutylmalonic ester and α-bromisovaleric ester. The resulting isopropylisobutylethane tricarboxylate,



$$\begin{array}{r}\mathrm{(CH_3)_2CH{-}CH_2{-}C(COOC_2H_5)_2} \\ \mathrm{(CH_3)_2{=}CH{-}CHCOOC_2H_5}\end{array},$$

saponified by means of alcoholic potash, gave, by subsequent loss of carbon dioxide, the substance under discussion.

2. From α-bromisobutylacetic ether and sodium malonic ester. The resulting isobutylethanetricarboxylate,



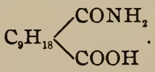
$$\begin{array}{r}\mathrm{(CH_3)_2CH{-}CH_2{-}CH{-}COOC_2H_5} \\ \mathrm{HC(COOC_2H_5)_2}\end{array},$$

was then converted into sodium salt, and this, treated with isopropyliodide, gives an isomeric isopropylisobutylethane tricarboxylate, which, on saponification and loss of carbon dioxide, gives *cis*-isopropylisobutylsuccinic acid.

First Method of Synthesis.—Eighty-three grams of isobutylmalonic ester were converted into the sodium salt by treatment in absolute ethereal solution with sodium wire. The sodium salt is very soluble in ether and is obtained, on removing the ether over sulphuric acid *in vacuo*, as a gelatinous, sticky mass. This was treated in sealed tubes with the theoretical amount of ethyl α-bromisovalerate, heating at first for six hours at 125° to 130° and then for eight hours at 140° to 150°. On pouring into water, extracting with ether, and fractionating *in vacuo*, 36 grams of isopropylisobutylethane tricarboxylate,[1] boiling at 175° to 180° at 14 mm. pressure,

[1] Cf. Bischoff : Ber. d. chem. Ges., 29, 976.

were obtained (there was a considerable forerunner). Heated for eight hours under a reversed condenser with 30 grams of caustic potash and 60 grams of alcohol, saponification took place, and the corresponding free acid was obtained as an oil, on extracting the acidified solution with ether. On heating to 240° it lost carbon dioxide and gave the anhydride of *cis*-isopropylisobutylsuccinic acid. It was dissolved in concentrated aqueous caustic potash. On acidifying, extracting with ether, etc., the crude acid obtained gradually solidified while standing over sulphuric acid *in vacuo*. It was now washed with low-boiling ligroin and purified by dissolving in glacial acetic acid and precipitating by addition of water. *cis*-Isopropylisobutylsuccinic acid is thus obtained in white, crystalline needles or plates, melting at 118° to 119°. The acid, which is quite soluble in acetone, acetic ether, benzene, and acetic acid, but very sparingly soluble in cold water, was not analyzed in the free state. It gives insoluble calcium and silver salts (analysis, see below). Especially characteristic is its behavior towards ammonia after heating to 240°, when anhydride formation probably takes place (the anhydride was not isolated). On addition of aqueous ammonia, solution takes place and on acidifying with sulphuric acid a very voluminous, white precipitate separates out. This is the amino acid,



$$C_9H_{18}\left\langle\begin{array}{l}CONH_2\\COOH\end{array}\right. .$$

It was purified by dissolving in acetone and precipitating with water. It formed fine, silky needles, melting at 145° to 146° (analysis, see second method of synthesis).

In a similar manner the corresponding anilido and *p*-toluido acids were obtained, *i. e.*, by treating the heated *cis*-acid with aniline and *p*-toluidine, respectively. The former melts at 149° to 150° (needles, from alcohol) and the latter at 156° to 157°.

The calcium salt of *cis*-isopropylisobutylsuccinic acid, obtained as a crystalline precipitate on adding a solution of the acid, carefully neutralized with ammonia, to concentrated, aqueous calcium chloride, gave the following analytical results, after drying at 140°.

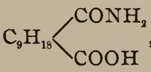
I. 0.3700 gram salt gave 0.0812 gram CaO.
II. 0.2208 gram salt gave 0.0481 gram CaO.

	Calculated for $CaC_{11}H_{18}O_4$.	Found.	
		I.	II.
Ca	15.75	15.67	15.55

The corresponding silver salt, made by double decomposition from the ammonium salt and silver nitrate, was obtained as a white, amorphous precipitate.

0.4160 gram salt, dried over H_2SO_4 *in vacuo*, gave 0.2080 gram Ag.

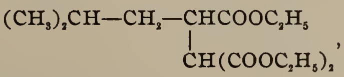
	Calculated for $C_{11}H_{18}O_4Ag_2$.	Found.
Ag	50.23	50.19

The silver salt of the amino acid,  $C_9H_{18}\begin{cases}CONH_2\\COOH\end{cases}$, melting-point 146°, was obtained by double decomposition reaction from the ammonium salt and silver nitrate as a white, gelatinous, amorphous precipitate.

0.2767 gram salt, dried over sulphuric acid *in vacuo*, gave 0.0949 gram Ag.

	Calculated for $C_{11}H_{20}O_3NAg$.	Found.
Ag	33.54	33.7

Second Method of Synthesis.—Isobutylacetic acid (b. p. 200° to 202°), made according to the directions of W. A. Noyes,[1] was converted into α-bromisobutylacetic ether (b. p. 99° to 102° at 17 mm. pressure), by the method of Bentley and Perkin.[2] One hundred and forty-two grams of the α-bromester were treated in sealed tubes with 56 grams of sodium malonic ester, heating first for five hours at 100° and then for sixteen hours at 135° to 140°. Thus 130 grams of α,α,β-isohexane tricarboxylate,



$$\begin{array}{l}(CH_3)_2CH-CH_2-CHCOOC_2H_5\\ \qquad\qquad\qquad\qquad\quad |\\ \qquad\qquad\qquad\qquad\quad CH(COOC_2H_5)_2\end{array},$$

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[1] J. Am. Chem. Soc., 18, 393.

[2] J. Chem. Soc. (London), 73, 49.

(b. p. 176° to 177° at 19 mm. pressure) were obtained.

0.2421 gram substance gave 0.5298 gram CO_2 and 0.1877 gram H_2O.

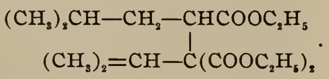
	Calculated for $C_{15}H_{26}O_6$.	Found.
C	59.80	59.71
H	8.55	8.62

A portion of the substance (10 grams) was saponified by means of alcoholic potash and converted by subsequent loss of carbon dioxide into isobutylsuccinic acid, which was found identical in its properties with those given in the literature. Another portion, 40 grams, was converted into the sodium salt by means of sodium in absolute ethereal solution. The salt, which is quite soluble in ether, is obtained on evaporation of the ether over sulphuric acid in a vacuum as an amorphous mass. It was heated in a sealed tube with 1.5 molecules of isopropyliodide, at first for two hours at 125° and then for ten hours at 140° to 150°. On working up the reaction-product, 20 grams of oil (b. p. 186° to 188° at 15 mm. pressure) were obtained. Analysis proved that the product was still not quite completely alkylated.

0.2094 gram substance gave 0.4772 gram CO_2 and 0.1721 gram H_2O.

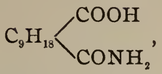
	Calculated for $C_{18}H_{32}O_6$.	Found.
C	62.8	62.01
H	9.3	9.18

The substance was, therefore, again treated with sodium and isopropyl iodide. A product, boiling from 188° to 190° at 15 mm. pressure, was now obtained which is obviously pure isopropylisobutylethane tricarboxylate,



$$\begin{array}{l}(CH_3)_2CH—CH_2—CHCOOC_2H_5 \\ \qquad\qquad\qquad\qquad\quad | \\ \qquad (CH_3)_2{=}CH—C(COOC_2H_5)_2\end{array} .$$

It was saponified with alcoholic potash and the resulting oily acid converted by heating to 240° with loss of carbon dioxide into the anhydride of *cis*-isopropylisobutylsuccinic acid. On adding aqueous ammonia and acidifying, the amino acid,



$$C_9H_{18}\begin{cases}COOH \\ CONH_2\end{cases},$$

mentioned above, separates out as a bulky precipitate. It was purified by dissolving in acetone and precipitating with ligroin. Fine needles, melting at 146°, and identical in all their properties with the corresponding product in the first method of synthesis, were obtained. The substance is soluble in alcohol and acetone, very slightly soluble in ether and chloroform, and practically insoluble in benzene and ligroin. Heated with lime or with concentrated aqueous potash, it gives off ammonia and is converted into *cis*-isopropylisobutylsuccinic acid melting at 118°. An analysis of the amino acid (an analysis of the silver salt is given above) gave the following results :

0.2163 gram substance gave 0.4868 gram CO_2 and 0.1937 gram H_2O.

0.2500 gram substance, heated with lime, required 11.5 cc. N/10 H_2SO_4 on titration.

	Calculated for $C_{11}H_{21}NO_3$.	Found.
C	61.39	61.35
H	9.76	9.95
N	6.51	6.44

Sodium Ethylate and Sodium Acetate Heated Alone and in the Presence of Carbon Monoxide.

A repetition of the experiment by Geuther and Fröhlich,[1] using a mixture of 380 grams of sodium ethylate and sodium acetate (equal molecules mixed intimately in a mortar) and passing carbon monoxide over the mass at 180° to 200° for four days of seven hours each, gave, besides 2 grams of a neutral oil and much formic and acetic acids, only 2 grams of a solid acid, melting from 165° to 172°, which could not be identified as mesitylenic acid. Two grams of normal butyric acid, boiling from 160° to 175°, were also obtained.

The following experiment proves that butyric acid is formed by simply heating the mixture of the acetate and ethylate, *i. e.*, without passing carbon monoxide over it: Two hundred and ninety grams of sodium ethylate and sodium acetate (equal molecules mixed intimately in a mortar) were heated for five days, of seven hours each, to 200° to 210°. No neutral products were found and 4 grams of butyric acid, boiling from 160° to 164°, were obtained. A portion of this was converted into the calcium salt and analyzed.

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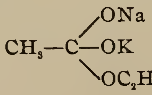
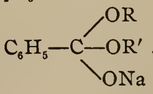
[1] *Loc. cit.*

0.3727 gram salt gave 0.2376 gram $CaSO_4$.

	Calculated for $CaC_8H_{14}O_4$.	Found.
Ca	18.68	18.75

Besides this, 2 grams of acid boiling from 165° to 195° were obtained, which probably contains some diethylacetic acid. No solid acid was obtained in this experiment.

It is likely that much more decisive results would have been obtained by adding 1 molecule of sodium acetate to an alcoholic solution of sodium ethylate. Subsequent removal of the alcohol in an atmosphere of hydrogen, at 200° to 210°, etc., must result in a partial or even complete interaction between the two ingredients. The following experiment makes this exceedingly probable: On mixing alcoholic solutions of sodium ethylate and potassium acetate, a very voluminous precipitate separates out at once in the cold. This is probably the ortho addition-product,[1]  $CH_3—C\begin{cases}ONa\\OK\\OC_2H_5\end{cases}$, corresponding to Claisen's orthobenzoic acid derivatives,[2]  $C_6H_5—C\begin{cases}OR\\OR'\\ONa\end{cases}$.

The Dissociation of Soaium Methylate.

One hundred grams of alcohol-free sodium methylate, prepared in the usual way, were heated in a distilling-flask in a bath, the temperature of which ranged from 260° to 400° during the course of the experiment. The distilling-flask was connected with a short condenser, an empty Bunsen wash-bottle with two tubes containing bromine and a gasometer. No olefine bromides were obtained. Fifteen liters of gas, proved by analysis to consist of 90 per cent hydrogen and 10 per cent marsh-gas, were obtained. The strongly-charred residue left in the distilling-flask was found to give off acetylene with water, as proved by its conversion into the silver and copper salt. Three liters of gas were thus obtained, which was found by analysis to consist of 30 per cent hydrogen and 70 per cent acetylene.

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[1] This product is now being investigated in the laboratory. J. U. NEF.

[2] Ber. d. chem. Ges., 20, 649.

The residue left in the distilling-flask after treatment with water consisted of free carbon and sodium carbonates. The proportion was found to be 12 grams of combined carbon to 8.5 grams of free carbon.

The formation of acetylene in small quantities, on treating the salt residue with water, proves that sodium acetylene, C_2Na_2, is one of the decomposition-products of sodium methylate by heat. This can readily be understood in view of the experiments of Nef.[1] Formaldehyde (or its addition-product $H_2C(ONa)_2$), which is formed by the interaction of the dissociation-products of sodium methylate, *i. e.*, of methylene with sodium hydroxide,

$$CH_2\rightrightarrows + 2H—ONa = CH_2(ONa)_2 + 2H,$$

gives, by dissociation, atomic carbon,

$$CH_2O \text{ or } CH_2(ONa)_2 = C \text{ and } H_2O \text{ or } 2NaOH.$$

The atomic carbon acts in part on the sodium hydroxide present to give free sodium, but in great part polymerizes to graphite and amorphous carbon. In this operation diatomic carbon,[2] C=C, is naturally first formed which unites in part with the sodium set free to give disodium acetylene,

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[1] Cf. Ann. Chem. (Liebig), **298**, 303 : **318**, 189 and 197. The marked physiological properties of aqueous formaldehyde solutions is due to the presence of atomic carbon particles formed by dissociation, $H_2C(OH)_2 \rightleftarrows H_2O + \begin{matrix}H\diagdown\\OH\diagup\end{matrix}\!C \rightleftarrows 2H_2O + C$, as has been pointed out by Nef in his lectures on organic chemistry for some years past.

[2] The formation of calcium carbide and of acetylene in the electric furnace or arc, respectively, is due to a partial dissociation of the graphite or amorphous carbon, C_x, into diatomic carbon, $C_x \rightleftarrows \frac{x}{2}(C:C)$, which then unites at once with the calcium or hydrogen atoms present to form calcium carbide or acetylene, respectively. J. U. NEF.

$$C_2 + Na_2 = C_2Na_2.$$

In conclusion, I desire to thank Dr. Nef for the assistance and encouragement he has given me in the course of my work.

REVIEWS.

NOTES ON METALLURGICAL ANALYSIS. Arranged for Students of Metallurgical Chemistry. Selected Methods for the Analysis of Iron and Steel, and of the Materials used in Their Manufacture, Including the Analysis of Gases, Fuels, Water for Boiler Supply, etc., together with Explanatory Notes on the Manipulation and Chemistry of the Various Processes. By NATHANIEL WRIGHT LORD, E.M., Professor of Metallurgy and Mineralogy at the Ohio State University, and Consulting Chemist of the Ohio Geological Survey. Second edition, rewritten, and greatly enlarged. Columbus, Ohio, 1903, Metallurgical Laboratory, Ohio State University.

The promise on the long title-page is fulfilled in the text. The student, who has worked through the analytical methods given, should be well qualified for practical work. Professor Lord explains and criticizes all of the familiar standard methods as well as many of the newer methods, and gives abundant literature references. He assumes in the student a knowledge of inorganic chemistry and qualitative analysis and some knowledge of quantitative analysis, and in the 222 pages of text no space is wasted on descriptions of reagents and common apparatus, as is so common in books on metallurgical chemistry. Professor Lord's work is so good that it should find frequent use. E. R.

ANALYTICAL CHEMISTRY. By F. P. TREADWELL, PH.D., Professor of Analytical Chemistry in the Polytechnic Institute of Zurich. Translated with the author's permission from the second German edition by WILLIAM T. HALL, S.B., Instructor in Chemistry, Massachusetts Institute of Technology. Volume I. Qualitative Analysis. First edition, first thousand. New York: John Wiley & Sons. 1903. pp. 463. Price, $3.00.

Professor Treadwell is widely known as a good chemist, teacher, and lecturer. This book is, as he says in the preface, "a somewhat amplified repetition" of his lectures on analytical chemistry. It is well written, interesting, well translated by Mr. Hall, and its appearance is creditable to the publishers. Of modern innovations, the author utilizes the law of mass action, the theory of electrolytic dissociation and hydrolysis, explaining their relations to analysis, and making special reference throughout the book in those places where these laws serve to made dark places clear.

The book will be a pleasant addition to a chemical library, and will doubtless be helpful and suggestive to students, but it is not necessary for them, for lectures in qualitative analysis involve much repetition and review of general chemistry, and only the most important analytical methods can be mentioned in such a course of lectures. So this book contains little which is not to be found in the larger text-books of chemistry, supplemented by the average laboratory manual, but it is too large, handsome, and costly to use in the laboratory, while the analytical methods given are too few for it to be used as a reference book. Nor can it supplant a text-book, for there is no mention of argon or helium, for example, the author very properly confining himself to those elements and compounds which occur in the ordinary scheme of instruction in qualitative analysis. E. R.

ANLEITUNG ZUR UNTERSUCHUNG DER FÜR DIE ZUCKERINDUSTRIE IN BETRACHT KOMMENDEN ROHMATERIALIEN, PRODUKTE, NEBENPRODUKTE, UND HILFSSUBSTANZEN. Sechste umgearbeitete und vermehrte Auflage. Herausgegeben von PROF. DR. R. FRÜHLING. Braunschweig: Friedrich Vieweg und Sohn.

This work of Dr. R. Frühling, of Braunschweig, has now reached its sixth edition. The book contains 505 pages, and treats in general of the chemistry of materials entering into the manufacture of beet sugar.

The first part is devoted to descriptions of the apparatus used in the optical and chemical analysis of sugar juice, sugars, molasses, sugar beets, limestones, water, and the other substances necessary to the manufacture of sugar from the sugar beet. The methods of analysis of these bodies are also given in sufficient detail. The rules for the analysis of sugar, adopted by the International Committee for the Unification of Sugar Analysis, which met in Paris in 1900, are also given.

This is the first edition of the work which discusses in full the necessity of polarizing sugar solutions at a standard temperature, or of correcting the polarizations if the temperatures differ from the standard. Both the method of Wiley and Schönrock are given, but the author fails to distinguish the different principles on which the correction factors of the two methods are ascertained. In the method of Wiley it is directed that the solutions be made up and polarized at the same temperature, while in the method of Schönrock it is directed that they be made up at the standard temperature and the correction is for a polarization at a different temperature.

The latest and best forms of polariscopic apparatus are described. The method of determining sugars in mixtures is given and elaborate tables for use in the chemical determination of sugars by the reduction of alkaline copper solutions are furnished. The various methods of ascertaining the richness of sugar beets designed for seed production are described.

An interesting feature of the work is the space it devotes to the residues of sugar manufactories, especially the disposal of the molasses. The increasing importance of molasses as a cattle food is recognized by a description of the methods of analyses of foods into which molasses enters. The growing importance of the sugar industry in the United States demands that works of this kind be placed at the disposal of chemists and engineers in order that the processes of manufacture may be conducted according to the most improved methods and with the greatest economy.

Dr. Frühling has devoted the greater part of his active life to the study of these problems, and this, the latest and largest edition of his work, will commend itself to all who are interested in the sugar industry. H. W. W.

AN INTRODUCTION TO THE STUDY OF THE COMPOUNDS OF CARBON OR ORGANIC CHEMISTRY. By IRA REMSEN, President of the Johns Hopkins University. Fourth revision. Boston : D. C. Heath & Co. 1903.

" The important advances that have been made in the field of organic chemistry during the past few years have made a thorough revision of this book necessary. The present edition gives the results of the revision. The principal changes and additions will be found in the chapters dealing with the sugars, stereoisomerism, the diazo compounds, and the terpenes. The treatment of the aromatic compounds is, in general, fuller than in the older editions. Although considerable has been added, the size of the volume has not been markedly increased, the difference between the last edition and the present being only about 50 pages. In addition to the changes indicated above, minor changes have been made throughout, and the author believes that the book is now fully in harmony with the present state of organic chemistry."—[Preface to the Fourth Revision.]

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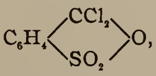
AMERICAN

CHEMICAL JOURNAL

FURTHER INVESTIGATIONS ON THE TWO ISOMERIC CHLORIDES OF ORTHOSULPHOBENZOIC ACID.

BY IRA REMSEN.

Since the last communications on this subject[1] work has been continued somewhat interruptedly, as other matters have claimed attention. That two isomeric chlorides of orthosulphobenzoic acid exist has been shown beyond any possibility of doubt. The relations between these chlorides have perhaps not yet been made entirely clear, but the study of the reactions of the two with a number of substances has brought to light many facts of interest that must be taken into account in dealing with the problem of isomerism presented by the chlorides. List and Stein[2] have shown that the substance described by Saunders[3] and myself, and later by McKee,[4] and myself and believed to be the pure unsymmetrical chloride,



$$C_6H_4\left\langle\begin{matrix}CCl_2\\SO_2\end{matrix}\right\rangle O,$$

with the melting-point 21° to 22°, is in reality "a mixture" of the chloride melting at 79° and another melting at 40°. This "mixture" has a constant melting-point that is not changed by repeated crystallizations. It crystallizes in definite form and presents the characteristics of a definite chemical compound. List and Stein also observed that the melting-point is not changed "durch wiederholtes Krystallisiren." The low-melting chloride used in the work treated of in the following articles was prepared by the method of List and Stein.

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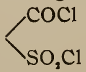
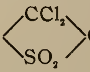
[1] This JOURNAL, **18**, 791, 794, 809, 819.

[2] Ber. d. chem. Ges., **31**, 1648.

[3] This JOURNAL, **17**, 352.

[4] *Ibid.*, **18**, 794.

The work has been extended to a nitro derivative of orthosulphobenzoic acid that happens to be comparatively easily obtainable. The corresponding isomeric chlorides containing the nitro group have been prepared and their reactions studied,[1] and the chlorides of parabromorthosulphobenzoic acid have been prepared and investigated. The results of this work will soon be communicated. The main point of interest connected with all this work is the peculiar character of the relation between the isomeric chlorides. Each one of any given pair of isomers is a definite substance with well-defined properties. One cannot be transformed into the other by any means thus far employed. If one is dissolved in any solvent that does not act chemically upon it, that one comes out of the solution again, and it retains its identity after repeated crystallizations. Nor can one be transformed into the other by heat. So far as the substances themselves are concerned, there is no reason for calling one the *stable* and the other the *unstable* variety. In their relations towards other substances, on the other hand, a marked difference is observed. The chloride of higher melting-point enters into reaction much less readily than that of lower melting-point. Hence, List and Stein[2] propose to call the former the *stable* and the latter the *unstable* chloride. As I have previously pointed out, it seems highly probable that one of the chlorides contains the group  $\left\langle\begin{matrix}COCl\\SO_2Cl\end{matrix}\right.$ and the other the group  $\left\langle\begin{matrix}CCl_2\\SO_2\end{matrix}\right\rangle O$; and, accordingly, I have called the one containing the former group the *symmetrical*, and the one containing the latter group the *unsymmetrical* chloride. I have also shown that the reactions of the chloride of orthosulphobenzoic acid that melts at 79° make it probable that this is the symmetrical variety, and the weight of evidence is also in favor of the conclusion that the chloride with the lower melting-point is the unsymmetrical variety. It must be confessed that the case is a difficult one to deal with, for the reason that, with some reagents, both chlorides give the same products, and these sometimes have the symmetrical and sometimes the unsymmetrical structure. If this were true of all reagents, the task would plainly be a hopeless one. List and Stein[1] hold that the facts do not justify any conclusion in regard to the structure of the chlorides. I still think that my former conclusions are justified. The reactions upon which I have relied are those with ammonia and those with aniline and similar bases. List and Stein agree with me in regard to the action of ammonia. It is established that the chloride melting at 79° reacts with ammonia in such a way as to form quantitively the ammonium salt of benzoic sulphinide,

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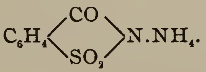
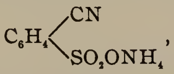
[1] Remsen and Gray: This JOURNAL, **19**, 496; Hollis: *Ibid.*, **23**, 233.

[2] *Loc. cit.*



$$C_6H_4\left\langle\begin{matrix}CO\\SO_2\end{matrix}\right\rangle N.NH_4.$$

On the other hand, the chloride with the lower melting-point, treated with the same reagent, yields principally the ammonium salt of orthocyanbenzenesulphonic acid,



$$C_6H_4\left\langle\begin{matrix}CN\\SO_2ONH_4\end{matrix}\right.,$$

together with a greater or smaller quantity of the ammonium salt of benzoic sulphinide. The quantity of the latter product depends upon the temperature. The lower the temperature the smaller the quantity. Under some conditions the ammonium salt of *o*-cyanbenzenesulphonic acid is the sole product, not even a trace of the sulphinide being formed.

The above facts, taken by themselves, lead clearly to the conclusion that the chloride melting at 79° has the symmetrical structure, and that the other chloride has the unsymmetrical structure. Accordingly, the reactions should be represented by these equations:

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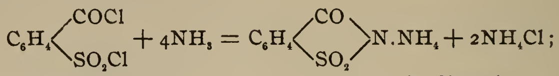
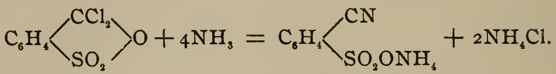
[1] *Loc. cit.*

I.


$$C_6H_4\left\langle\begin{array}{l}COCl\\SO_2Cl\end{array}\right. + 4NH_3 = C_6H_4\left\langle\begin{array}{l}CO\\SO_2\end{array}\right\rangle N.NH_4 + 2NH_4Cl;$$

Symmetrical chloride. Ammonium salt of benzoic sulphinide.

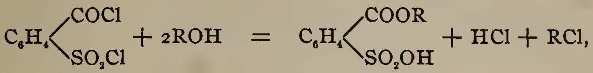
II.


$$C_6H_4\left\langle\begin{array}{l}CCl_2\\SO_2\end{array}\right\rangle O + 4NH_3 = C_6H_4\left\langle\begin{array}{l}CN\\SO_2ONH_4\end{array}\right. + 2NH_4Cl.$$

Unsymmetrical chloride. Ammonium salt of orthocyanbenzenesulphonic acid.

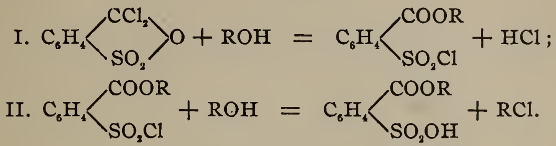
The action of ammonia on the two chlorides has been further investigated in this laboratory by Mr. R. M. Bird. In general, the earlier results have been confirmed. The unsymmetrical, or high-melting, chloride gives only the sulphinide. The pure, unsymmetrical, or low-melting chloride gives mainly the ammonium salt of *o*-cyanbenzenesulphonic acid with more or less of the ammonium salt of benzoic sulphinide, depending upon the conditions of the experiments. When very dilute (1 : 20) aqueous ammonia was used the reaction took place very slowly and only a trace of the sulphinide was obtained. This was detected by the taste and could not be isolated. With stronger ammonia (1 : 3) the amount of sulphinide obtained formed from 4 to 20 per cent of the total product. About the same results were obtained when the most concentrated ammonia was used. On the other hand, when the chloride was dissolved in anhydrous ether or chloroform, and dry ammonia gas passed into the solution, only the ammonium salt of *o*-cyanbenzenesulphonic acid was obtained. The product did not have a sweet taste, a fact that shows conclusively that not even a trace of the sulphinide was formed.

The further study of the action of alcohols upon the two chlorides which has been carried out by Mr. R. M. Bird has confirmed the results previously obtained and has brought to light some facts not heretofore established. The principal facts to be noted in this connection are these, that the high-melting chloride yields acid esters with alcohols,



$$C_6H_4\left\langle\begin{matrix}COCl\\SO_2Cl\end{matrix}\right. + 2ROH = C_6H_4\left\langle\begin{matrix}COOR\\SO_2OH\end{matrix}\right. + HCl + RCl,$$

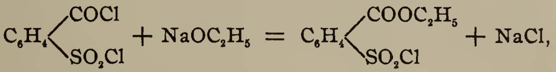
while the low-melting chloride yields, first, ester chlorides, and these in turn give the acid esters:



$$\text{I. } C_6H_4\left\langle\begin{matrix}CCl_2\\SO_2\end{matrix}\right\rangle O + ROH = C_6H_4\left\langle\begin{matrix}COOR\\SO_2Cl\end{matrix}\right. + HCl;$$

$$\text{II. } C_6H_4\left\langle\begin{matrix}COOR\\SO_2Cl\end{matrix}\right. + ROH = C_6H_4\left\langle\begin{matrix}COOR\\SO_2OH\end{matrix}\right. + RCl.$$

It appears, however, that when the high-melting chloride, in solution in anhydrous ether, is treated with a solution of sodium ethylate in ethyl alcohol the ester chloride is formed,

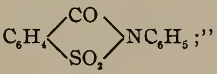


$$C_6H_4\left\langle\begin{matrix}COCl\\SO_2Cl\end{matrix}\right. + NaOC_2H_5 = C_6H_4\left\langle\begin{matrix}COOC_2H_5\\SO_2Cl\end{matrix}\right. + NaCl,$$

though this reaction requires further study.

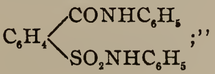
In regard to the reactions with aniline, List and Stein state that they worked exactly as we did, but obtained different results.

In an earlier article by Kohler and myself[1] it is stated that (1) "the product of the action of aniline upon the dry, high-melting chloride is symmetrical orthosulphobenzanil, which has the structure represented by the formula



$$C_6H_4\left\langle\begin{matrix}CO\\SO_2\end{matrix}\right\rangle NC_6H_5\,;''$$

(2) that "the product of the action of aniline upon the solid chloride in an emulsion with water is symmetrical orthosulphobenzanilide, which has the structure



$$C_6H_4\left\langle\begin{matrix}CONHC_6H_5\\SO_2NHC_6H_5\end{matrix}\right.\;;''$$

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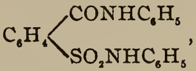
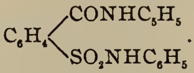
[1] This JOURNAL, 17, 330.

and (3) that "the product of the action of aniline upon the liquid (low-melting) chloride of orthosulphobenzoic acid is the infusible anilide."

Later, McKee[1] repeated the experiments of Kohler and found that the high-melting chloride gives only the anilide of the structure  $C_6H_4 \left\langle \begin{array}{l} CONHC_6H_5 \\ SO_2NHC_6H_5 \end{array} \right.$, and none of the infusible anilide. He found, however, that the low-melting chloride used by him (melting at 21° to 22°) gives both anilides.

Evidence has previously been presented that goes to show that the anilide obtained from the high-melting chloride is the symmetrical one represented by the formula



$$C_6H_4 \left\langle \begin{array}{l} CONHC_5H_5 \\ SO_2NHC_6H_5 \end{array} \right. .$$

As the other anilide was not obtained from this chloride, it was concluded that the high-melting chloride has the symmetrical structure as indicated by the reaction with ammonia. The fact that two anilides, or, at least, two substances of the same composition as the anilide are formed from the low-melting (liquid) chloride, appears to be analogous to the fact that two isomeric products are formed when ammonia and water act upon this same chloride.

On treating a mixture of the two chlorides with aniline some of the anil was always formed.

The main fact that appeared to be established by these earlier investigations is the formation of the symmetrical anilide alone from the high-melting chloride. List and Stein state that each of the chlorides gives all three of the products above referred to, that is to say, the symmetrical anilide, the unsymmetrical anilide, and the anil. If this be true, my former argument based on the action of the chlorides towards aniline is of no value.

Though feeling certain that there was no error in my work, I have repeated it with the aid of Mr. W. B. Holmes, and have found that when the high-melting chloride is treated with aniline in the presence of water no trace of the unsymmetrical anilide is formed, the products being the symmetrical anilide and the anil. On the other hand, when the low-melting chloride is treated in the same way, the products are the two anilides and no anil.

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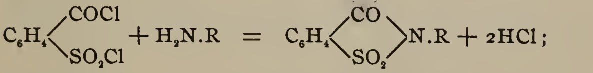
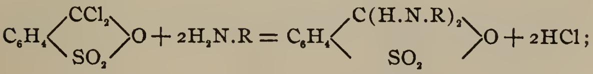
[1] This Journal, 18, 804.

If, however, either of the chlorides is dissolved in ether and then treated with aniline, all three of the products already referred to are formed as claimed by List and Stein. The method employed by us consists in adding the aniline to an emulsion of the chloride in a relatively large amount of cold water. Reaction then takes place without perceptible evolution of heat.

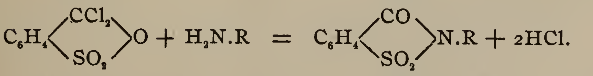
Mr. F. E. Clark has studied the action of methylamine, dimethylamine, and ethylamine upon the two chlorides, and has shown that methylamine and ethylamine give the corresponding esters of benzoic sulphinide when they act upon the symmetrical chloride, and that with the unsymmetrical chloride they give mainly unsymmetrical, substituted diamides, together with small quantities of the esters of benzoic sulphinide :



$$C_6H_4\left\langle\begin{array}{l}COCl\\SO_2Cl\end{array}\right. + H_2N.R = C_6H_4\left\langle\begin{array}{c}CO\\SO_2\end{array}\right\rangle N.R + 2HCl;$$



$$C_6H_4\left\langle\begin{array}{c}CCl_2\\SO_2\end{array}\right\rangle O + 2H_2N.R = C_6H_4\left\langle\begin{array}{c}C(H.N.R)_2\\SO_2\end{array}\right\rangle O + 2HCl;$$



$$C_6H_4\left\langle\begin{array}{c}CCl_2\\SO_2\end{array}\right\rangle O + H_2N.R = C_6H_4\left\langle\begin{array}{c}CO\\SO_2\end{array}\right\rangle N.R + 2HCl.$$

He has shown, further, that with dimethylamine the high-melting chloride gives a symmetrical product, or at least that only one product is formed, and this has presumably the symmetrical structure. The low-melting chloride, on the other hand, does not give a definite product when treated with dimethylamine.

List and Stein,[1] in studying the action of phenol upon the two chlorides, deny the correctness of the statements of Remsen and McKee[1] to the effect that when the symmetrical chloride is treated with phenol the diphenyl ester,

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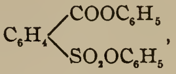
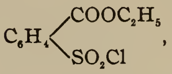
[1] *Loc. cit.*



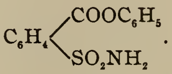
$$C_6H_4\left\langle\begin{matrix}COOC_6H_5\\SO_2OC_6H_5\end{matrix}\right.,$$

and the phenyl ester chloride,



$$C_6H_4\left\langle\begin{matrix}COOC_2H_5\\SO_2Cl\end{matrix}\right.,$$

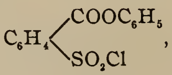
are formed. The existence of the latter in the product was not shown by isolating it, but by treating the mass with ammonia, when the chloride was converted into the phenyl ester of *o*-sulphaminebenzoic acid,



$$C_6H_4\left\langle\begin{matrix}COOC_6H_5\\SO_2NH_2\end{matrix}\right..$$

List and Stein were unable, for some reason, to obtain this compound and they make the following sweeping statement in regard to it: "Hingegen, haben wir uns trotz der sorgfältigsten Versuche vergeblich bemüht, den von Remsen dargestellten *o*-Sulfaminbenzoësäureester zu fassen. Nach unseren Versuchen scheint der Ester überhaupt nicht existenzfähig zu sein."

The work of Remsen and McKee has been repeated by Mr. R. E. Humphreys and the results confirmed. It is true that the sulphone chloride,



$$C_6H_4\left\langle\begin{matrix}COOC_6H_5\\SO_2Cl\end{matrix}\right.,$$

does not react with ammonia directly, but when a mixture of the symmetrical chloride and phenol is treated with ammonia the phenyl ester of *o*-sulphaminebenzoic acid is easily formed and is identical with the substance described under this name by Remsen and McKee. The low-melting chloride gives the same products with phenol as the high-melting chloride.

Mr. K. G. Falk has repeated the work of List and Stein on the reduction of the two chlorides and has obtained the same results. It is undoubtedly true that the high-melting, or symmetrical, chloride gives sulphobenzid,

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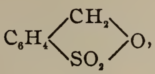
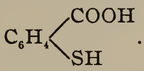
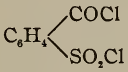
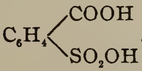
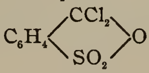
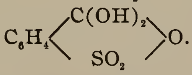
[1] This JOURNAL, 18, 794.

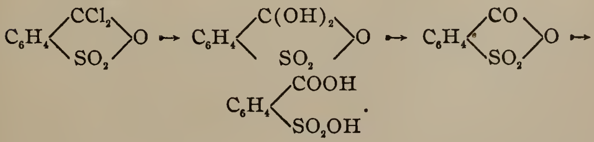

$$C_6H_4\left\langle{CH_2 \atop SO_2}\right\rangle O,$$

when reduced, while the low-melting, or unsymmetrical, chloride gives thiosalicylic acid,


$$C_6H_4\left\langle{COOH \atop SH}\right. .$$

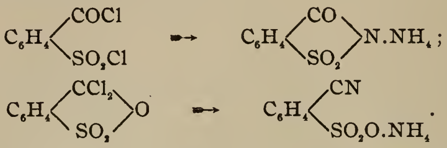
The reactions that must be taken into consideration in speculating upon the structure of the two chlorides are those with water, alcohols, phenols, ammonia, the substituted ammonias, and nascent hydrogen.

1. Water gives but one product, orthosulphobenzoic acid, whether the high-melting or the low-melting chloride is used. This is quite in accordance with what we should expect. A compound of the formula  $C_6H_4\left\langle{COCl \atop SO_2Cl}\right.$ would, of course, give one of the formula  $C_6H_4\left\langle{COOH \atop SO_2OH}\right.$. A compound of the unsymmetrical structure,  $C_6H_4\left\langle{CCl_2 \atop SO_2}\right\rangle O$, would first give a product of the structure  $C_6H_4\left\langle{C(OH)_2 \atop SO_2}\right\rangle O$. This is probably an unstable form which would lose water and yield the anhydride as an intermediate product. But this would at once take up water and form the acid. The changes involved are indicated below :


$$C_6H_4\left\langle{CCl_2 \atop SO_2}\right\rangle O \rightarrow C_6H_4\left\langle{C(OH)_2 \atop SO_2}\right\rangle O \rightarrow C_6H_4\left\langle{CO \atop SO_2}\right\rangle O \rightarrow C_6H_4\left\langle{COOH \atop SO_2OH}\right. .$$

The action of water, therefore, throws no light upon the problem of the structure of the two chlorides.

2. The action of ammonia upon the two chlorides is of especial interest. Under proper conditions, the high-melting chloride gives only the ammonium salt of the sulphinide, and the low-melting chloride gives only the ammonium salt of *o*-cyanbenzenesulphonic acid :

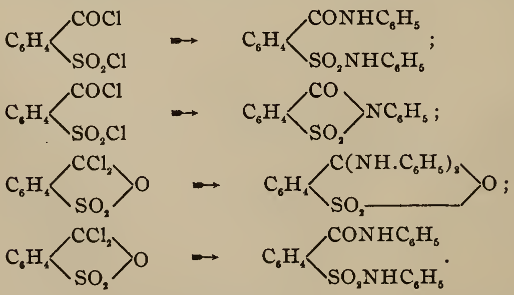


$$C_6H_4\left\langle\begin{matrix}COCl\\SO_2Cl\end{matrix}\right. \longrightarrow C_6H_4\left\langle\begin{matrix}CO\\SO_2\end{matrix}\right\rangle N.NH_4\,;$$

$$C_6H_4\left\langle\begin{matrix}CCl_2\\SO_2\end{matrix}\right\rangle O \longrightarrow C_6H_4\left\langle\begin{matrix}CN\\SO_2O.NH_4\end{matrix}\right. .$$

These reactions are unequivocal and, if taken by themselves, show clearly that the high-melting chloride has the symmetrical, and that the low-melting chloride has the unsymmetrical, structure.

3. The reactions with aniline are not quite as clear as those with ammonia, but in general terms they confirm the conclusion to which those with ammonia point. An emulsion of aniline in cold water gives, with the high-melting chloride, the symmetrical anilide and the anil, while, under the same circumstances, the low-melting chloride gives the unsymmetrical anilide and the symmetrical anilide :



$$C_6H_4\left\langle\begin{matrix}COCl\\SO_2Cl\end{matrix}\right. \longrightarrow C_6H_4\left\langle\begin{matrix}CONHC_6H_5\\SO_2NHC_6H_5\end{matrix}\right. ;$$

$$C_6H_4\left\langle\begin{matrix}COCl\\SO_2Cl\end{matrix}\right. \longrightarrow C_6H_4\left\langle\begin{matrix}CO\\SO_2\end{matrix}\right\rangle NC_6H_5\,;$$

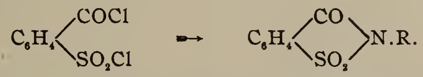
$$C_6H_4\left\langle\begin{matrix}CCl_2\\SO_2\end{matrix}\right\rangle O \longrightarrow C_6H_4\left\langle\begin{matrix}C(NH.C_6H_5)_2\\SO_2\end{matrix}\right\rangle O\,;$$

$$C_6H_4\left\langle\begin{matrix}CCl_2\\SO_2\end{matrix}\right\rangle O \longrightarrow C_6H_4\left\langle\begin{matrix}CONHC_6H_5\\SO_2NHC_6H_5\end{matrix}\right. .$$

In the case of the unsymmetrical chloride, the proportion of the unsymmetrical anilide formed is considerably larger than that of the symmetrical anilide.

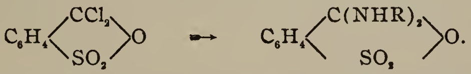
These facts are in accordance with the view that the high-melting chloride has the symmetrical structure, and the low-melting chloride the unsymmetrical structure. The formation of the symmetrical anilide, together with the unsymmetrical anilide, from the low-melting chloride, is a symptom of a general tendency possessed by this chloride to yield, to some extent, symmetrical products.

4. The action of methyl- and ethylamines and of dimethylamine is of the same general kind as that of aniline, though with some differences, as has been pointed out. The high-melting chloride gives esters of benzoic sulphinide with methyl- and ethylamines:



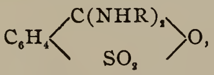
$$C_6H_4\left<\begin{matrix}COCl\\SO_2Cl\end{matrix}\right. \longrightarrow C_6H_4\left<\begin{matrix}CO\\SO_2\end{matrix}\right>N.R.$$

The low-melting chloride gives a diamide which is probably analogous to the infusible unsymmetrical dianilide:



$$C_6H_4\left<\begin{matrix}CCl_2\\SO_2\end{matrix}\right>O \longrightarrow C_6H_4\left<\begin{matrix}C(NHR)_2\\SO_2\end{matrix}\right>O.$$

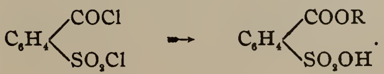
This reaction furnishes no evidence for or against the formulas of the two chlorides, as it has not been proved that the product above represented by the formula



$$C_6H_4\left<\begin{matrix}C(NHR)_2\\SO_2\end{matrix}\right>O,$$

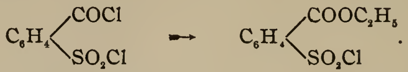
really has the unsymmetrical structure. To be sure, it is infusible like the unsymmetrical dianilide, but that is not strong evidence of its structure.

5. With alcohols the high-melting chloride does not react easily in the cold. When the solution is boiled or allowed to stand for some time the product is the acid ester:



$$C_6H_4\left<\begin{matrix}COCl\\SO_2Cl\end{matrix}\right. \longrightarrow C_6H_4\left<\begin{matrix}COOR\\SO_2OH\end{matrix}\right..$$

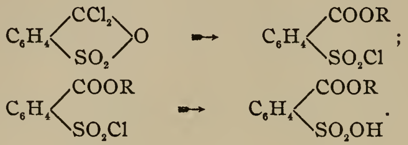
By treating an alcoholic solution of the high-melting chloride with an alcoholic solution of sodium ethylate an ester chloride is formed :



$$C_6H_4\left\langle\begin{array}{l}COCl\\SO_2Cl\end{array}\right. \rightarrow C_6H_4\left\langle\begin{array}{l}COOC_2H_5\\SO_2Cl\end{array}\right. .$$

The same reaction takes place with sodium methylate.

On the other hand, the low-melting chloride reacts very readily with alcohols and gives the ester chlorides which, by further action of the alcohols, give the acid esters :



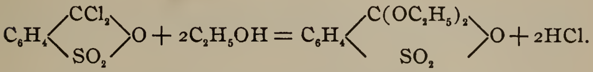
$$C_6H_4\left\langle\begin{array}{l}CCl_2\\SO_2\end{array}\right\rangle O \rightarrow C_6H_4\left\langle\begin{array}{l}COOR\\SO_2Cl\end{array}\right. ;$$

$$C_6H_4\left\langle\begin{array}{l}COOR\\SO_2Cl\end{array}\right. \rightarrow C_6H_4\left\langle\begin{array}{l}COOR\\SO_2OH\end{array}\right. .$$

Both chlorides then give the same products with alcohols and these products have the symmetrical structure. To be sure, the symmetrical chloride with an alcohol alone does not give the intermediate ester chloride, but gives the acid ester. This appears to be due to the fact that this chloride reacts with difficulty with the alcohols. It is necessary to boil the solution and then, of course, the product is the acid ester, for, if the ester chloride were first formed, it would, under the conditions of the experiment, be converted into the acid ester. When, however, the reaction is aided by the addition of sodium alcoholate, the ester chloride is first formed.

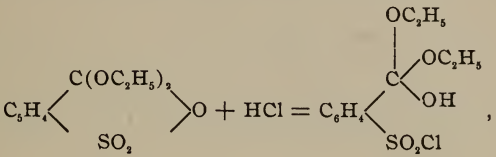
The fact that ester chlorides are easily obtained from the low-melting chloride by treating them with alcohols, when taken by itself, suggests that this chloride has the symmetrical structure. But the fact cannot be taken by itself. The low-melting chloride has certainly not the same structure as the high-melting chloride and the evidence in favor of the symmetrical structure for the latter seems to me to be conclusive. It is clear, however, that the low-melting chloride with some reagents gives symmetrical products, though it generally gives unsymmetrical products.

The formation of ester chlorides from a substance of the unsymmetrical structure is, further, easily accounted for without assuming any mysterious "molecular rearrangement." The first action of the alcohol is probably that represented by the equation



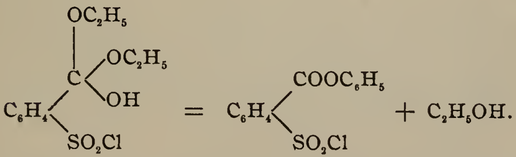
$$C_6H_4\left\langle\begin{matrix}CCl_2\\SO_2\end{matrix}\right\rangle O + 2C_2H_5OH = C_6H_4\left\langle\begin{matrix}C(OC_2H_5)_2\\SO_2\end{matrix}\right\rangle O + 2HCl.$$

The anhydride would then take up hydrochloric acid:

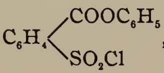
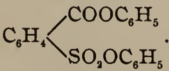


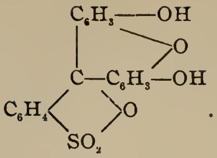
$$C_5H_4\left\langle\begin{matrix}C(OC_2H_5)_2\\SO_2\end{matrix}\right\rangle O + HCl = C_6H_4\left\langle\begin{matrix}\overset{OC_2H_5}{C}\left\langle\begin{matrix}OC_2H_5\\OH\end{matrix}\right.\\SO_2Cl\end{matrix}\right. ,$$

and the product thus formed would lose alcohol and give the ester chloride



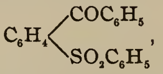
$$C_6H_4\left\langle\begin{matrix}\overset{OC_2H_5}{C}\left\langle\begin{matrix}OC_2H_5\\OH\end{matrix}\right.\\SO_2Cl\end{matrix}\right. = C_6H_4\left\langle\begin{matrix}COOC_6H_5\\SO_2Cl\end{matrix}\right. + C_2H_5OH.$$

6. With ordinary phenol the reactions are somewhat different from those with the alcohols. It gives the same products with both chlorides. These are the phenyl ester chloride,  $C_6H_4\left\langle\begin{matrix}COOC_6H_5\\SO_2Cl\end{matrix}\right.$, and the diphenyl ester,  $C_6H_4\left\langle\begin{matrix}COOC_6H_5\\SO_2OC_6H_5\end{matrix}\right.$. Plainly no light is thrown upon the structure of the two chlorides by these reactions. Curiously enough, with resorcinol both chlorides give the same unsymmetrical product, sulphonfluoresceïn:



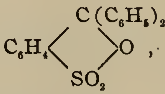
These reactions also do not help to determine the structural relations of the two chlorides.

7. With benzene and aluminium chloride both chlorides give the same symmetrical product,

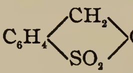
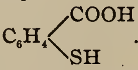
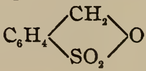
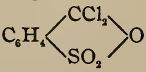


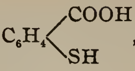
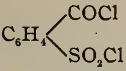
$C_6H_4<^{COC_6H_5}_{SO_2C_6H_5}$,

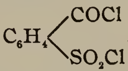
but under some conditions the low-melting chloride gives a little of another product, probably the isomeric, unsymmetrical compound,

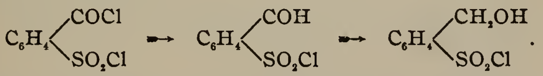
,

though this is by no means certain.

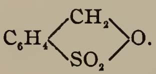
8. The reduction of the two chlorides seems at first sight to show that the high-melting chloride is unsymmetrical and the low-melting chloride symmetrical. The high-melting chloride gives sulphobenzid, , and the low-melting chloride gives thiosalicylic acid,  $C_6H_4<^{COOH}_{SH}$. If these were the only facts to guide us, we should probably conclude that the chloride that yields sulphobenzid, , by reduction must have the symmetrical structure, , and we could easily reconcile ourselves to the belief that the chlo-

ride that yields thiosalicylic acid,  $C_6H_4\left<\begin{matrix}COOH\\SH\end{matrix}\right.$, must have the symmetrical structure,  $C_6H_4\left<\begin{matrix}COCl\\SO_2Cl\end{matrix}\right.$, though this connection does not appear as clear as that between sulphobenzid and the unsymmetrical chloride.

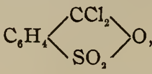
It seems to me, however, that all the other reactions are more easily explained by assuming that the high-melting chloride is symmetrical and the low-melting chloride unsymmetrical. The question then naturally suggests itself: Can the reactions of the two chlorides with reducing agents be explained in any other plausible way than that adopted by List and Stein and outlined above? I think they can, and, indeed, I think the other explanation is, to say the least, fully as rational as that given by List and Stein. Take first a compound of the symmetrical structure,  $C_6H_4\left<\begin{matrix}COCl\\SO_2Cl\end{matrix}\right.$. It is well known that the group COCl is more easily reduced than the group SO_2Cl. We should, therefore, expect that the symmetrical chloride would first yield an aldehyde and then an alcohol, thus:

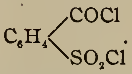

$$C_6H_4\left<\begin{matrix}COCl\\SO_2Cl\end{matrix}\right. \rightarrow C_6H_4\left<\begin{matrix}COH\\SO_2Cl\end{matrix}\right. \rightarrow C_6H_4\left<\begin{matrix}CH_2OH\\SO_2Cl\end{matrix}\right..$$

The alcohol would, however, easily lose hydrochloric acid and give the corresponding anhydride, sulphobenzid,


$$C_6H_4\left<\begin{matrix}CH_2\\SO_2\end{matrix}\right>O.$$

According to this the formation of sulphobenzid from the symmetrical chloride is not only possible but at least as probable as its formation from a chloride of the unsymmetrical structure.

Turning now to the reduction of the unsymmetrical, or low-melting, chloride. The product is thiosalicylic acid. How can the formation of this substance be explained on the assumption that the chloride has the unsymmetrical structure? The low-melting chloride reacts very easily with water as with most other reagents. It seems probable that before the reduction could be effected the chloride would be converted partly into the anhydride and partly into the acid. The reduction of these would then, in turn, be likely to give thiosalicylic acid. An attempt was made to test this view experimentally, and apparently small quantities of thiosalicylic acid were obtained when the anhydride and the acid were reduced. The results were, however, not very satisfactory. Not much, if any, weight can be attached to these experiments. But, leaving them entirely out of consideration, it seems to me that it is as easy to explain the formation of thiosalicylic acid from a chloride of the formula  $C_6H_4\left\langle\begin{matrix}CCl_2\\SO_2\end{matrix}\right\rangle O$, as from one of the formula



$$C_6H_4\left\langle\begin{matrix}COCl\\SO_2Cl\end{matrix}\right. .$$

The details of the experimental work are given in the following articles.

I. THE ACTION OF AMMONIA AND OF ALCOHOLS AND ALCOHOLATES UPON THE CHLORIDES OF ORTHOSULPHOBENZOIC ACID.[1]

BY R. M. BIRD.

The action of aqueous ammonia of various dilutions and at various temperatures upon the low-melting chloride was first studied, and also the action of the dry gas upon solutions of the chloride in anhydrous ether and chloroform, as well as upon the dry chloride.

Very Dilute Aqueous Ammonia.—The solution was made by adding 20 volumes of water to 1 volume of a solution thoroughly saturated with ammonia at the temperature of hydrant water, about 18° C. The unsymmetrical chloride, either in solution in ether or dry, was treated with this ammonia at 0° and at the ordinary temperature. Two experiments were conducted at the former and four at the latter temperature. In all cases it required four or five days to complete the reaction, regardless of the amounts of chloride used, provided, of course, proportional quantities of ammonia were added. The products were, in all cases, ammonium orthocyanbenzenesulphonate, a trace of the ammonium salt of benzoic sulphinide and ammonium chloride. The cyanbenzenesulphonate was practically the only organic product of the reaction, for the amount of sulphinide was too small to be detected except by a slightly sweet taste of the solution. In no case could a precipitate be obtained on acidifying with hydrochloric acid, even though the acidified solution was allowed to stand for days. It was allowed to stand because it requires time for a complete precipitation of benzoic sulphinide from the solutions of its salts; and it was found, further, that adding concentrated hydrochloric acid to the extent of one-third the volume of the solution gave the quickest and most complete precipitation of benzoic sulphinide when this was formed, as in the experiments with stronger ammonia. The effect of the low temperature was only to retard the reaction and this was not marked. The following equation expresses the reaction:

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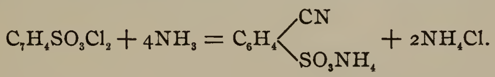
[1] From the author's dissertation submitted, June, 1901, to the Board of University Studies of the Johns Hopkins University in conformity with the requirements for the degree of Doctor of Philosophy.



$$C_7H_4SO_3Cl_2 + 4NH_3 = C_6H_4\left\langle\begin{matrix}CN\\ SO_3NH_4\end{matrix}\right. + 2NH_4Cl.$$

Action of Strong Ammonia (*1 : 3*).—In carrying out the experiments with ammonia of this strength (1 volume saturated to 3 volumes water) at 0°, both the ethereal solution of the chloride and the ammonia solution were cooled to the temperature of melting ice and the ammonia added slowly, with constant stirring, to the chloride immersed in an ice-bath, where it remained until all the chloride was dissolved in the ammoniacal solution. In other experiments sometimes ethereal solutions and sometimes the dry chloride were used, and the temperature rose considerably during the reaction. The principal product was the same with this dilution of ammonia as in all other cases, but here a considerable amount of the chloride was changed to the ammonium salt of benzoic sulphinide. The following table gives the amounts of benzoic sulphinide formed in several experiments :

Temperature.	Amount of chloride taken. Grams.	Amount of sulphinide obtained. Gram.	Per cent of chloride changed to sulphinide.
0°	0.7492	0.1169	20.3
0°	0.5998	0.0842	18.2
0°	2.1112	0.1377	8.5
..	1.3978	0.0519	4.1
..	1.4362	0.0514	4.6
..	2.4384	0.2649	14.1
..	1.9301 (dry)	0.2191	14.8

The method used to precipitate the sulphinide is not strictly quantitative, but an effort was made to keep the conditions the same and thus make the results comparable. The filtrates did not taste sweet. I am unable to give any reason for the great variations.

Action of Concentrated Ammonia.—In a number of experiments the ordinary concentrated and saturated solutions of ammonia were used, and the products were the same as with the 1 : 3 solution. The reaction was very vigorous, and with the saturated solution it was explosive. In only one experiment was an effort made to influence the temperature of the reaction and in this the chloride and ammonia solutions were heated quickly in a water-bath at 80° C. The benzoic sulphinide obtained from three experiments was weighed and the yield was as follows :

Amount of chloride taken. Grams.	Amount of sulphinide obtained. Gram.	Per cent of chloride changed to sulphinide.
1.2799 (dry)	0.1564	15.9
1.0873 (eth. sol.)	0.1388	16.6
0.5825 "	0.0737	16.4

This agrees fairly well with several results of the action of 1 : 3 ammonia.

Action of Water-free Ammonia.—The ammonia was passed through two drying cylinders filled with soda-lime and allowed to act upon the unsymmetrical chloride—either dry or in solution in anhydrous ether or chloroform. When the chloride was dry it had to be broken up with a rod as fast as acted upon, because of a hard coating which protected the enclosed chloride. The heat of reaction was marked in all cases. In one experiment with 0.5 gram dissolved in about 40 cc. of ether the temperature at the beginning of the reaction was 20° ; during the first half minute of the rapid passing of the gas it fell to 19°, and as soon as the products, which are insoluble in ether, began to form, the temperature rose rapidly to 28°—during a minute or two—and then fell to 14° at the end of thirty minutes. The room temperature was about 20°. In all the experiments with the unsymmetrical chloride, a very small quantity resisted the action of ammonia, and it was to insure the conversion of this that the gas was passed for so long a time. Experiments were carried out with dilute ethereal solutions cooled to 0° in an ice-bath, the solution being rapidly stirred while a slow current of gas was conducted into it, with the temperature held at 18°.5—that of a hydrant water-bath—and also upon the dry chloride and upon concentrated and dilute ethereal solutions, with no attempt to regulate the temperature. In no case could we obtain any product but ammonium cyanbenzenesulphonate. It did not even taste of benzoic sulphinide. As a check upon our test for other substances than the cyan salt, the amount of that substance was determined, as near as is possible with a substance so hard to separate from its by-products. The method used by List and Stein[1] was found to be the most satisfactory.

2.5519 grams of the chloride were dissolved in anhydrous ether and dry ammonia gas passed through the solution until the reaction was certainly complete. The ether was allowed to evaporate spontaneously, and a water solution of the residue was heated to 60° and treated with freshly precipitated silver oxide until there was no further precipitation of silver chloride. The filtered solution was then treated with freshly prepared ammonium sulphide until no more silver sulphide came down, and the resulting solution was evaporated to dryness on a water-bath, dried by standing over sulphuric acid, and weighed. The weight was somewhat more than that called for by a quantitative conversion of the chloride into ammonium *o*-cyanbenzenesulphonate. This, together with the failure to find any other product, was considered conclusive evidence that the whole reaction is to be expressed by the equation

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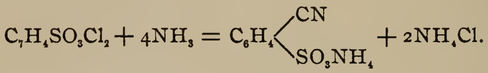
[1] Ber. d. chem. Ges., 31, 1649.



$$C_7H_4SO_3Cl_2 + 4NH_3 = C_6H_4\begin{cases} CN \\ SO_3NH_4 \end{cases} + 2NH_4Cl.$$

Experiments with Benzoic Sulphinide.—To see how far the conditions of the experiments with the unsymmetrical chloride affected the salt of benzoic sulphinide that might be formed in the reaction, pure benzoic sulphinide was subjected to the same treatment, with these results :

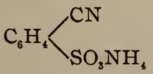
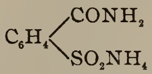
Sulphinide taken. Grams.	Sulphinide recovered. Grams.	Loss. Per cent.
1.8564	1.8064	2.7
1.9481	1.9067	2.1

The results of a third experiment may as well be recorded, although the conditions tending to hydrolysis were in no wise comparable to those under which ammonia acted upon the chloride : 1.3375 grams of pure benzoic sulphinide were dissolved in boiling hot water and one-third of its volume of concentrated hydrochloric acid immediately added. After standing several hours the precipitate was filtered, dried, and weighed. It showed a loss of 8.4 per cent.

Action of Ammonia on the Symmetrical Chloride—The action of dry and aqueous ammonia upon the symmetrical chloride was also studied where experiments parallel to those with the unsymmetrical seemed desirable, and the results were in entire accordance with those of work previously done in this laboratory. The speed of reaction as compared with that of the unsymmetrical was very slow. The results of the only experiments in which the amount of benzoic sulphinide precipitated by hydrochloric acid was determined are as follows :

Strength of ammonia.	Amount of chloride taken. Gram.	Amount of sulphinide obtained. Gram.	Per cent of chloride changed.
1 : 3	0.3535(dry)	0.2551	93.7
Saturated	0.8613(ether)	0.5679	85.6
Dry	0.7439 "	0.5027	87.8

The amount of sulphinide, which cannot be recovered by this method, represented, of course, a large percentage of the small quantity of chloride used in the above experiments, and hence the variation from the theoretical does not necessarily signify that anything else was formed. It is not unlikely that the same cause of variation operated here as in the case of the unsymmetrical chloride and 1 : 3 ammonia. It was impossible to detect any other substance than the ammonium salt of benzoic sulphinide and ammonium chloride in the product.

Ammonium o-Cyanbenzenesulphonate and Ammonium o-Carbaminebenzenesulphonate.—For the sake of completeness the properties of ammonium *o*-cyanbenzenesulphonate are given here, although it has been fully described by those who have obtained it previously. It crystallizes from alcoholic solutions in white botryoidal masses of needles. The second form of crystals, rosettes of transparent needles, described by Karslake, was not obtained.[1] It is very soluble in water and hot alcohol, moderately soluble in cold alcohol, and insoluble in dry ether. I found it easier to hydrolyze it to *o*-sulphobenzoic acid than my interpretation of most remarks on this subject led me to think. The hydrolysis was effected by boiling for ten hours a solution acidified with hydrochloric acid. In how short a time this transformation can be effected was not determined. The passage from the substance of the formula  $C_6H_4\begin{cases}CN\\SO_3NH_4\end{cases}$ to one of the formula  $C_6H_4\begin{cases}CONH_2\\SO_2NH_4\end{cases}$ was repeatedly accomplished by simply evaporating to dryness on a water-bath the solutions from which benzoic sulphinide had been precipitated by hydrochloric acid. Water alone does not hydrolyze it.

The ammonium carbaminebenzenesulphonate, obtained from the cyan salt, crystallized out in two forms, white needles and large, thick crystals (the long axis of one was nearly a centimeter in length), behaving exactly like the ammonium cyanbenzenesulphonate described by Karslake, and like his substance also, the thick crystals recrystallized as needles.[1] In every instance in which the melting-point of the carbamine salt was taken the first crystals melted gradually from 250° to 260°, and when recrystallized they melted at 256° to 257°.[2]

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[1] This JOURNAL, 18, 820.

Much difficulty was experienced in getting ammonium *o*-cyanbenzenesulphonate free from the last traces of ammonium chloride, yet it was accomplished by repeatedly recrystallizing it from absolute alcohol. But the potassium salt can be obtained without difficulty. It is only necessary to add a saturated solution of potassium carbonate to a solution containing the products formed by the action of ammonia on the chloride even if it is moderately dilute, when a fine, white, crystalline powder is precipitated. The potassium salt crystallizes easily from a water solution in beautiful, thick, square-ended, transparent needles, radiating from centers. This was also found to be a ready method of following the process of hydrolysis, as the potassium salt of orthocarbaminesulphonic acid only crystallizes from very concentrated water solutions and is not precipitated by potassium carbonate, while, as has been said, the potassium cyan salt can be obtained from quite dilute solutions by rubbing the sides of the beaker.

Action of Alcohols and Alcoholates.

Earlier work of Remsen and Dohme,[3] Karslake,[4] and List and Stein[1] has shown that the two chlorides react with alcohol first to form ester chlorides which by further action of the alcohols pass over into the corresponding ester acids:

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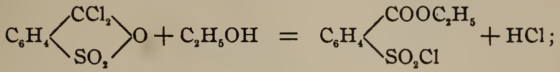
[1] This JOURNAL, **18**, 821.

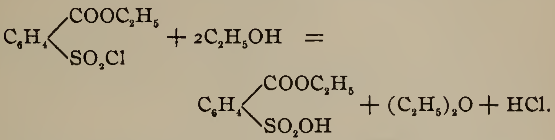
[2] Karslake gave 219° to 220° as the melting-point of the substance he obtained on heating an acidified solution of the cyan salt (*Ibid.*, **18**, 825). Fahlberg and Barge described a salt which they proved to be ammonium orthocyanbenzenesulphonate as thin, transparent needles, melting at 255° to 256° (Ber. d. chem. Ges., **22**, 759). F. D. Wilson described it as large plates melting at 262° to 263° (Dissertation, J. H. U., 1899, p. 26). M. D. Sohon described it as needles melting at 256° to 257° (This JOURNAL, **20**, 269). Karslake's substance did not lose weight when heated, but all the others described it as losing water of crystallization when heated to 125° C. The salt which I obtained agreed with the latter.

[3] This JOURNAL, **11**, 341.

[4] *Ibid.*, **18**, 825.

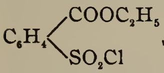
I. 

$$C_6H_4\begin{matrix}CCl_2\\SO_2\end{matrix}O + C_2H_5OH = C_6H_4\begin{matrix}COOC_2H_5\\SO_2Cl\end{matrix} + HCl;$$

II. 

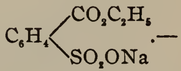
$$C_6H_4\begin{matrix}COOC_2H_5\\SO_2Cl\end{matrix} + 2C_2H_5OH = C_6H_4\begin{matrix}COOC_2H_5\\SO_2OH\end{matrix} + (C_2H_5)_2O + HCl.$$

The ester chloride is easily formed from the unsymmetrical chloride; less easily from the symmetrical chloride. When, however, the symmetrical chloride is dissolved in anhydrous ether and a slightly warm emulsion of sodium ethylate (2 mols. ethylate to 1 mol. chloride) in absolute alcohol added to the solution, reaction takes place smoothly until about one-half of the alcoholate has been added, when it stops and cannot easily be carried farther. An oil was obtained from the solution that had the general properties of the ester chloride,

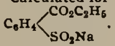


$C_6H_4\begin{matrix}COOC_2H_5\\SO_2Cl\end{matrix}$, though the evidence that it is this substance is not conclusive.

Sodium Orthosulphonate of Ethyl Benzoate,



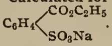
$C_6H_4\begin{matrix}CO_2C_2H_5\\SO_2ONa\end{matrix}$.—This was obtained by dissolving the symmetrical chloride in ethyl alcohol and treating it with an alcoholic emulsion of sodium ethylate and allowing it to stand for two or three hours. The solution became slightly warm. After heating the purified salt to constant weight it was analyzed:



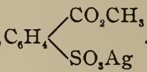
	Calculated for $C_6H_4\begin{matrix}CO_2C_2H_5\\SO_2Na\end{matrix}$.	Found.
Na	9.12	9.38

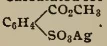
[1] Ber. d. chem. Ges., 31, 1659.

The same compound was obtained by treating dry sodium ethylate with an excess of the *o*-sulphone chloride of ethyl benzoate made from the unsymmetrical chloride, and extracting the product with ethyl alcohol. After drying to constant weight the salt gave :

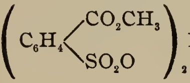
	Calculated for  $C_6H_4{<}\begin{matrix}CO_2C_2H_5\\SO_3Na\end{matrix}.$	Found.
Na	9.12	9.20

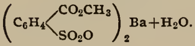
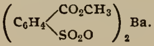
It crystallizes in beautiful, transparent, colorless leaves and elongated hexagons with beveled edges.

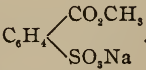
Silver Orthosulphonate of Methyl Benzoate,  $C_6H_4{<}\begin{matrix}CO_2CH_3\\SO_3Ag\end{matrix}$. — On analysis this salt gave the following figures :

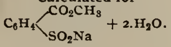
	Calculated for  $C_6H_4{<}\begin{matrix}CO_2CH_3\\SO_3Ag\end{matrix}.$	Found.	
		I.	II.
Ag	33.41	33.76	33.10

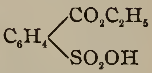
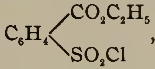
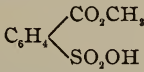
Barium Orthosulphonate of Methyl Benzoate,

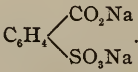
 $\left(C_6H_4{<}\begin{matrix}CO_2CH_3\\SO_2O\end{matrix}\right)_2$ Ba.—Analysis gave :

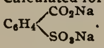
	Air-dried crystals.		After heating to constant weight.	
	Calculated for  $\left(C_6H_4{<}\begin{matrix}CO_2CH_3\\SO_2O\end{matrix}\right)_2 Ba+H_2O.$	Found.	Calculated for  $\left(C_6H_4{<}\begin{matrix}CO_2CH_3\\SO_2O\end{matrix}\right)_2 Ba.$	Found.
Ba	23.46	23.63	24.20	24.40

Sodium Orthosulphonate of Methyl Benzoate,  $C_6H_4{<}\begin{matrix}CO_2CH_3\\SO_3Na\end{matrix}.$ —Dry unsymmetrical chloride was added gradually to a saturated methyl alcoholic solution of sodium methylate and the gelatinous product filtered with suction through a platinum cone. It was evaporated by a current of dry air and recrystallized from methyl alcohol and from water several times. At first it crystallized in long, transparent, colorless needles, but on standing a few hours they changed completely to cubes and irregular crystals, looking as if the needles had been broken up. No other product was discovered. It was analyzed for sodium, carbon, hydrogen, and water of crystallization.

	Calculated for  $C_6H_4\left\langle\begin{array}{l}CO_2CH_3\\SO_2Na\end{array}\right. + 2.H_2O.$	Found.
Na	8.40	8.47
C (mean)	35.00	35.03
H "	4.00	3.80
H_2O	13.10	12.73

It is thus seen that the acid of the formula  $C_6H_4\left\langle\begin{array}{l}CO_2C_2H_5\\SO_2OH\end{array}\right.$ was obtained from the symmetrical chloride and sodium ethylate, and from the chloride  $C_6H_4\left\langle\begin{array}{l}CO_2C_2H_5\\SO_2Cl\end{array}\right.$, formed from the unsymmetrical chloride. The corresponding methyl ester of the formula  $C_6H_4\left\langle\begin{array}{l}CO_2CH_3\\SO_2OH\end{array}\right.$ was obtained from both chlorides and boiling methyl alcohol, and from the unsymmetrical chloride and sodium methylate.

Neutral Sodium Salt of o-Sulphobenzoic Acid,  $C_6H_4\left\langle\begin{array}{l}CO_2Na\\SO_3Na\end{array}\right.$.-- The dry crystals of the *o*-sulphone chloride of methyl benzoate were treated with a saturated methyl alcoholic solution of sodium methylate in small excess. The reaction was so vigorous that the alcohol boiled. The solution was filtered, extracted with ether and methyl alcohol, and the residue dissolved in water. Out of this came beautiful rosettes of transparent, colorless needles, which, when analyzed for sodium, gave:

	Calculated for  $C_6H_4\left\langle\begin{array}{l}CO_2Na\\SO_3Na\end{array}\right.$.	Found.
Na	18.80	19.22

Unidentified Products.

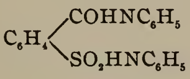
(*a*) Small quantities of dry unsymmetrical chloride and dry sodium ethylate (in the proportion of 1 molecule of the former to 2 of the latter) were mixed and ground fine in a mortar, the intention being to dissolve the mixture and eliminate as far as possible any action due to an excess of one or the other. Something called me off for perhaps ten minutes, and when I again touched the mixture with the pestle an explosion took place which resembled that of powder in an open vessel. Dense, white fumes with a peculiar and suffocating odor were given off, and a dry, light-brown mass remained, resembling crushed lava. The mortar was made hot through and through. The material was extracted with anhydrous ether and nothing obtained. Extraction with anhydrous alcohol yielded a little oil. Very concentrated ammonia was added to this oil and the excess of ammonia boiled off, but the solution did not become sweet. It was boiled with water, and on adding silver nitrate a white precipitate was formed, but this dissolved on boiling and did not coagulate, hence it was not silver chloride. There was not enough for further study. After extracting with alcohol, the residue dissolved in water, forming a neutral, amber-colored solution which, when evaporated in a desiccator, yielded dirty-looking crystals, which were apparently nothing but impure sodium chloride.

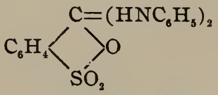
(*b*) A saturated solution of sodium methylate in methyl alcohol was added to dry, unsymmetrical chloride. The reaction was explosive. By immersing in hot water and passing a rapid current of dry air over it, the solution was evaporated to dryness and then extracted with dry ether. On evaporating off the ether an oil appeared which soon solidified. This was dissolved in methyl alcohol and evaporated down. It strongly resisted crystallizing, but on putting it in a freezing-mixture it came down quickly in diamond-shaped crystals, which melted at 38° to 39°. This was recrystallized three times without change in the melting-point, and the final product was well washed with water. Heating for two hours at 50° to 55° caused it to lose 1.01 per cent in weight. When absorbed in water the distillate gave the reaction for methyl alcohol. It is insoluble in cold water, but readily soluble in hot water, alcohol, and ether. When boiled with water it showed no acid properties, but when silver nitrate was added silver chloride was precipitated. After boiling with dilute aqueous ammonia the solution had a faintly sweet taste. On treating an ethereal solution with dry ammonia, ammonium chloride was precipitated, and from the ethereal solution some crystals were obtained, which melted gradually from 38° to 85°, apparently in two stages. They were slightly soluble in cold water, but easily soluble in hot water, ether, and alcohol. On attempting to recrystallize them the first time, a small quantity did not pass into solution, and this was found to melt at 132° to 135°. The ethereal solution of the rest was again treated, for thirty minutes, with ammonia gas, and after evaporation an oil remained and a few crystals like those above. The oil solidified in a freezing-mixture but again melted at the room temperature. I was unable to get a pure product out of the little that I had to work with.

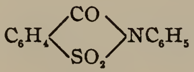
II. ACTION OF ANILINE UPON THE CHLORIDES OF ORTHOSULPHOBENZOIC ACID.

BY W. B. HOLMES.

The action of aniline on these chlorides has been the subject of numerous investigations in this laboratory. Three products have been isolated, a symmetrical anilide, an unsymmetrical anilide, and an anil. These have been clearly shown to have the following formulas :


Symmetrical anilide.


Unsymmetrical anilide.


Anil.

It was found that when aniline was added to an emulsion of the symmetrical chloride in a large amount of cold water and the reaction allowed to proceed slowly, only the symmetrical anilide and the anil were formed. With the unsymmetrical chloride, under similar conditions, only the two anilides were obtained, but a much larger percentage of the unsymmetrical anilide. These facts form one of the chief arguments for the assignment of the symmetrical and unsymmetrical formulas to the chlorides melting at 79° and 40°, respectively.

List and Stein[1] have recently tried the action of aniline on these chlorides. They brought the chloride and aniline together in a cold ethereal solution and obtained from each chloride all three products. They therefore claimed that the action of aniline on the chlorides affords no good grounds for assigning the symmetrical or unsymmetrical structure to either chloride. In view of their criticism a careful study of the action of aniline on each chloride was made under different conditions.

The relative amounts of the products formed depends largely upon the method employed for bringing the aniline and chloride together. The temperature at which the reaction takes place has a large influence upon the results. Either chloride, when heated with aniline alone, gives a mixture of all three products, the reaction being very violent in the case of the unsymmetrical chloride. When the symmetrical chloride is dissolved in anhydrous ether or chloroform, and aniline added, no reaction takes place. If this solution is heated on a water-bath, reaction takes place only when the ether or chloroform has been driven off. This is equivalent to heating the chloride and aniline together and then all three products are obtained. When the unsymmetrical chloride is dissolved in anhydrous ether or chloroform and aniline added, reaction takes place at once and all three products are obtained.

The best method is to add the aniline to an emulsion of the chloride in a large amount of cold water. Reaction takes place slowly without the evolution of heat. With the symmetrical chloride only the symmetrical anilide and anil are obtained, while with the unsymmetrical chloride both anilides are obtained but with a much larger percentage of the unsymmetrical anilide. The following results confirm the previous work done in this laboratory.

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[1] Ber. d. chem. Ges., **31**, 1648.

Action of Aniline upon the Symmetrical Chloride.—Three grams finely powdered chloride were placed in an Erlenmeyer flask with about 150 cc. of water. Aniline, in the proportion of 4 molecules of aniline to 1 of the chloride was then added and the contents of the flask vigorously shaken. At first there was no apparent reaction, the chloride simply dissolving in the aniline. After the lapse of three or four hours the aniline solution gradually solidified. The solid mass was then broken up and more aniline added. The resulting viscous mass was allowed to stand for two days with occasional shaking. The temperature of the water throughout the experiment varied little from 14°.

Hydrochloric acid was then added, the contents of the flask transferred to a mortar, and thoroughly ground up to remove the excess of aniline. The filtrate was evaporated and examined for the unsymmetrical anilide. If present, this substance would appear in the filtrate, as it is sparingly soluble in water and is not decomposed by hydrochloric acid. No trace of the unsymmetrical anilide could be obtained from the filtrates in a large number of experiments.

The residue was then treated with a dilute solution of sodium hydroxide. The undissolved precipitate consisted only of the anil. When the filtrate was acidified with hydrochloric acid only the symmetrical anilide was precipitated. From this precipitate and filtrate no trace of the unsymmetrical anilide could be obtained. The products of the reaction were only the anil and the symmetrical anilide. The chloride unaccounted for in the results was hydrolyzed to orthosulphobenzoic acid.

	Chloride used. Grams.	Total product. Grams.	Anil. Grams.	Symmetrical anilide. Grams.
1	3	3.19	1.96	1.23
2	3	3.15	1.80	1.35
3	3	3.20	1.94	1.26
4	3	3.24	1.98	1.26
5	3	3.36	2.01	1.35

	Chloride converted to anil. Grams.	Chloride converted to symmetrical anilide. Gram.	Chloride not accounted for. Gram.
1	1.81	0.84	0.30
2	1.66	0.91	0.43
3	1.79	0.85	0.36
4	1.83	0.85	0.32
5	1.85	0.91	0.24

Action of Aniline upon the Unsymmetrical Chloride.—The same method of procedure was employed in these experiments, except that the flasks were kept in ice-water for several hours after the experiment had started. Reaction took place much more quickly than with the symmetrical chloride. The aniline solution became solid in a very short time. The solid mass was then broken up and more aniline added. The viscous mass was allowed to stand for two days with occasional shaking. Hydrochloric acid was then added, the contents transferred to a mortar and thoroughly ground up to remove the excess of aniline. From the filtrate, part of the unsymmetrical anilide was obtained. The precipitate dissolved completely in a dilute solution of sodium hydroxide, showing that there was no anil formed. Hydrochloric acid precipitated a mixture of the anilides. The precipitate was washed with a large amount of water to remove the unsymmetrical anilide. When a constant weight had been obtained the product, when crystallized from alcohol, gave only the symmetrical anilide. The products of the reaction were only the symmetrical and unsymmetrical anilides, but with a much larger percentage of the unsymmetrical product. The chloride unaccounted for in the following results was probably hydrolyzed to orthosulphobenzoic acid.

	Chloride used. Grams.	Total product. Grams.	Symmetrical anilide. Grams.	Unsymmetrical anilide. Grams.
1	3	3.81	1.56	2.25
2	3	3.70	1.42	2.28
3	3	3.75	1.45	2.30
4	3	3.78	1.49	2.29
5	3	3.86	1.55	2.31

	Chloride converted to symmetrical anilide. Grams.	Chloride converted to unsymmetrical anilide. Grams.	Chloride not accounted for. Gram.
1	1.05	1.53	0.42
2	0.96	1.55	0.49
3	0.98	1.56	0.46
4	1.01	1.56	0.43
5	1.05	1.58	0.37

III. THE ACTION OF ALIPHATIC AMINES ON THE CHLORIDES OF ORTHOSULPHOBENZOIC ACID.[1]

BY FRIEND E. CLARK.

The action of ammonia and of aromatic amines upon the chlorides of orthosulphobenzoic acid has been studied in this laboratory, but the action of the aliphatic amines has not yet been investigated. In view of the remarkable relationship between the two chlorides, the study of their conduct under a variety of conditions is important. This investigation has to deal with their conduct towards methylamine, ethylamine, and dimethylamine.

The methyl- and dimethylamines were obtained from the corresponding hydrochlorides by treating their concentrated solutions with solid potassium hydroxide. In most of the experiments the employment of the dry amines was necessary. The drying of the gases was accomplished by passing them through one or more Peligot tubes, filled with pulverized sodium or potassium hydroxide. In cases where the anhydrous gas was not needed, the amine was passed directly into a vessel containing the chloride, or into water and afterwards used in the form of the aqueous solution.

Ethylamine was obtained from Kahlbaum, Berlin, in anhydrous condition, sealed in stout glass vessels. As the liquid amine was needed only in a few experiments, it was kept in the form of a 20 per cent aqueous solution, from which the free base was liberated as desired by adding solid potash.

Action of Methylamine on the Symmetrical Chloride of Orthosulphobenzoic Acid.—Substituted ammonias of the aromatic series yield two classes of compounds according to the conditions of the reactions. Aniline, for example, gives the dianilide and the anil. Methylamine and the symmetrical chloride, on the other hand, form one compound only, namely, the methyl ester of benzoic sulphinide, which corresponds to the anil obtained with aniline.

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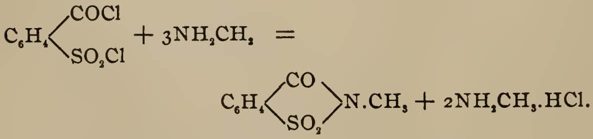
[1] From the dissertation of the author, submitted June, 1902, to the Board of University Studies of the Johns Hopkins University in conformity with the requirements for the degree of Doctor of Philosophy.

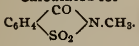
Dry methylamine was conducted into a solution of the symmetrical chloride in anhydrous ether. Immediately there appeared a white precipitate, that in every instance in which the temperature of the solution was kept below 25° C. and the flow of amine properly regulated, had a crystalline structure. Considerable difficulty was experienced in securing the proper conditions for the successful performance of the experiment. For example, even though the temperature of the solution of the chloride was lowered to 10° C., the temperature would rise very rapidly and the product be gummy, if the amine was allowed to pass into it rapidly. Methylamine hydrochloride, which was always one of the products of the reaction, was almost wholly precipitated from the solution, carrying down varying amounts of the ester with it. It was expedient to allow the ether to evaporate at ordinary laboratory temperatures. The mixture, which, under most favorable conditions, consisted of a white, flocculent mass, was transferred to a funnel and washed a few times with cold water in order to remove the methylamine hydrochloride. The residue was crystallized from alcohol and analyzed, and found to be the methyl ester of benzoic sulphinide. The reaction between the amine and symmetrical chloride can be represented by the equation :



$$C_6H_4{<}^{COCl}_{SO_2Cl} + 3NH_2CH_3 = C_6H_4{<}^{CO}_{SO_2}{>}N.CH_3 + 2NH_2CH_3.HCl.$$

0.2121 gram substance gave 0.2595 gram $BaSO_4$.
0.1149 gram substance gave 0.1394 gram $BaSO_4$.
0.0928 gram substance gave 0.1131 gram $BaSO_4$.

0.1354 gram substance gave 0.0083 gram N.
0.1312 gram substance gave 0.2326 gram CO_2.
0.1312 gram substance gave 0.0439 gram H_2O.

	Calculated for  $C_6H_4\left\langle\begin{matrix}CO\\SO_2\end{matrix}\right\rangle N.CH_3$.	Found.				
		I.	II.	III.	IV.	V.
C	48.68	....	....	....	....	48.34
H	3.53	....	....	....	....	3.24
N	7.07	....	....	....	6.13	....
S	16.26	16.89	16.65	16.73	....	....

The sulphur had to be determined by the method of Liebig. Many attempts were made to oxidize the ester with fuming nitric acid, according to the method of Carius, at temperatures as high as 350° C. Almost invariably a portion of the substance would resist the action of the acid. The nitrogen was determined by the Kjeldahl method.

Methyl benzoic sulphinide is slightly soluble in hot water, melting to a colorless oil, and practically insoluble in cold water. It is quite soluble in ether, more sparingly in absolute alcohol. From ethyl alcohol it crystallizes in fine needles; from a mixture of alcohol and water (about a 60 per cent solution) in large prisms terminating in pyramidal faces. The ester can be most easily obtained in pure crystalline condition by dissolving it in hot alcohol and adding warm water until the solution becomes cloudy, then heating on a water-bath until complete solution ensues, and allowing it to cool slowly. It is not sweet. It melts at 129° C.

Methyl benzoic sulphinide has been previously obtained by Remsen and Palmer[1] by heating the silver salt of the sulphinide with methyl iodide. Its melting-point is given by them as 128° to 129°.

Behavior of Methyl Benzoic Sulphinide in the Presence of Acids and Alkalies.—When boiled with the ester for twelve or fourteen hours, aqueous hydrochloric acid hydrolyzed it, forming the acid methylammonium salt of orthosulphobenzoic acid, which crystallized in radiating needles. One determination of sulphur indicated a compound of the formula

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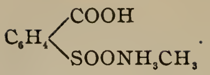
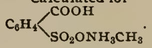
[1] This JOURNAL, 8, 226.



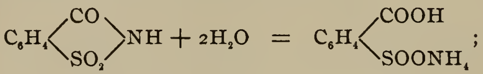
$$C_6H_4\left\langle\begin{matrix}\mathrm{COOH}\\ \mathrm{SOONH_3CH_3}\end{matrix}\right. .$$

0.2145 gram substance gave 0.2152 gram $BaSO_4$.

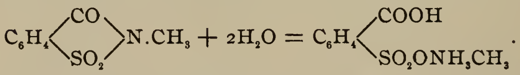
	Calculated for  $C_6H_4\left\langle\begin{matrix}\mathrm{COOH}\\ \mathrm{SO_2ONH_3CH_3}\end{matrix}\right.$.	Found.
S	13.74	13.79

When the acid methylammonium salt is heated with potassium hydroxide, neutral potassium orthosulphobenzoate and methylamine are formed. The acid potassium salt of orthosulphobenzoic acid is precipitated on the addition of hydrochloric acid to the aqueous solution of the neutral potassium salt.

The formation of the acid methylammonium salt of orthosulphobenzoic acid is in every way analogous to the action of hydrochloric acid on benzoic sulphinide:

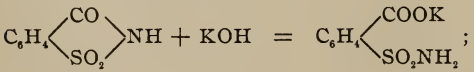


$$C_6H_4\left\langle\begin{matrix}\mathrm{CO}\\ \mathrm{SO_2}\end{matrix}\right\rangle NH + 2H_2O = C_6H_4\left\langle\begin{matrix}\mathrm{COOH}\\ \mathrm{SOONH_4}\end{matrix}\right. ;$$

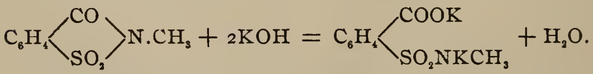


$$C_6H_4\left\langle\begin{matrix}\mathrm{CO}\\ \mathrm{SO_2}\end{matrix}\right\rangle N.CH_3 + 2H_2O = C_6H_4\left\langle\begin{matrix}\mathrm{COOH}\\ \mathrm{SO_2ONH_3CH_3}\end{matrix}\right. .$$

Just as benzoic sulphinide is converted into orthosulphaminebenzoic acid by treating it with dilute potassium hydroxide, so the methyl ester is hydrolyzed to orthomethylsulphaminebenzoic acid:



$$C_6H_4\left\langle\begin{matrix}\mathrm{CO}\\ \mathrm{SO_2}\end{matrix}\right\rangle NH + KOH = C_6H_4\left\langle\begin{matrix}\mathrm{COOK}\\ \mathrm{SO_2NH_2}\end{matrix}\right. ;$$

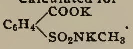


$$C_6H_4\left\langle\begin{matrix}\mathrm{CO}\\ \mathrm{SO_2}\end{matrix}\right\rangle N.CH_3 + 2KOH = C_6H_4\left\langle\begin{matrix}\mathrm{COOK}\\ \mathrm{SO_2NKCH_3}\end{matrix}\right. + H_2O.$$

One essential difference is to be noted, however. Aqueous alkalies do not effect the transformation in the latter case, alcoholic alkalies being necessary, and even then five or six hours' heating is required for the complete hydrolysis. It is of interest to note also that the alkali metals form the dimetallic salts, while the metals of the alkaline earths replace only the hydrogen of the carboxyl group.

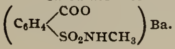
Potassium orthomethylsulphaminebenzoate crystallizes from alcohol in small plates. It is extremely soluble in water and alcohol, insoluble in petroleum ether.

0.1875 gram substance gave 0.1121 gram K_2SO_4.

	Calculated for  $C_6H_4\left\langle\begin{matrix}COOK\\SO_2NKCH_3\end{matrix}\right.$.	Found.
K	26.27	26.35

Barium hydroxide and the methyl ester give the barium salt of orthomethylsulphaminebenzoic acid. It is so soluble in water and alcohol that no crystals of it were obtained. From a mixture of benzene and ligroin an amorphous powder was obtained, from which two determinations of barium were made.

0.3014 gram substance gave 0.1281 gram $BaSO_4$.

	Calculated for  $\left(C_6H_4\left\langle\begin{matrix}COO\\SO_2NHCH_3\end{matrix}\right.\right)Ba$.	Found.
Ba	24.29	25.01

Preparation of Orthomethylsulphaminebenzoic Acid from Orthotoluenesulphone Methylamide. — Orthotoluenesulphone chloride was treated with a strong aqueous solution of methylamine. In the presence of a large excess of the amine, the toluenesulphone methylamide remains in semi-solid condition, so that one is quite easily misled in regard to the end of the reaction. The solution was cooled with ice-water and the amide separated by filtration. Orthotoluenesulphone methylamide was found to be insoluble in cold water, slightly insoluble in hot water, quite soluble in absolute alcohol, but from the last it did not crystallize in good condition. It is furthermore soluble in acetone and chloroform, thin, striated plates crystallizing from the former (m. p. 73° to 75° C.). The methylamide was found to be quite insoluble in cold benzene and almost insoluble in cold ligroin. A mixture of the two solvents gave the best results.

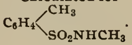
If the proper amount of ligroin is added to a solution of the amide in benzene, the amide comes out in the form of beautiful, colorless needles after one crystallization. Slow crystallization gives plates; rapid crystallization gives needles. The melting-point of both products is 74° to 75° C.

I. 0.1969 gram substance gave, by Liebig's method, 0.2510 gram $BaSO_4$.

II. 0.2033 gram substance gave, by Liebig's method, 0.2550 gram $BaSO_4$.

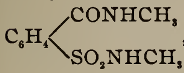
III. 0.1956 gram substance gave 0.3739 gram CO_2 and 0.1038 gram H_2O.

IV. 0.2216 gram substance gave 0.4186 gram CO_2 and 0.1191 gram H_2O.

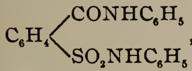
	Calculated for  $C_6H_4\langle^{CH_3}_{SO_2NHCH_3}$.	Found.			
		I.	II.	III.	IV.
S	17.31	17.45	16.92	....	....
C	51.77	....	....	52.12	51.51
H	6.06	....	....	5.94	6.01

The oxidation of the amide with potassium permanganate in alkaline solution gave rise to the formation of a small amount of the potassium salt of orthomethylsulphaminebenzoic acid, which, when acidified with hydrochloric acid at the ordinary temperature, passed to the methyl ester of benzoic sulphinide. However, when the temperature of the solution was lowered to about 10° C., the acid added cautiously, and the resulting solution allowed to evaporate slowly, orthomethylsulphaminebenzoic acid crystallized from the solution in small, radiating needles. The acid has no constant melting-point. It begins to soften at 70° C. and is not completely reduced to a clear liquid below 126° C. If the temperature is kept at the latter point for some minutes, then allowed to fall slowly, the product remaining in the tube will melt at 127° to 129° C., which indicates the formation of methyl benzoic sulphinide from orthomethylsulphaminebenzoic acid by the loss of 1 molecule of water.

Action of Aqueous Methylamine on the Symmetrical Chloride.—When a 20 per cent solution of methylamine in water is added to the pure symmetrical chloride of orthosulphobenzoic acid, reaction begins at the ordinary temperature, with the formation of methyl benzoic sulphinide and methylamine hydrochloride. At low temperatures a second compound is formed. This crystallizes in needles (m. p. 74° C.) and is probably the symmetrical dimethylamide of orthosulphobenzoic acid,



$C_6H_4\left\langle\begin{matrix}CONHCH_3\\SO_2NHCH_3\end{matrix}\right.$, analogous to the symmetrical dianilide,

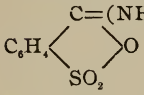


$C_6H_4\left\langle\begin{matrix}CONHC_6H_5\\SO_2NHC_6H_5\end{matrix}\right.$, which has been fully described by other investigators. The product melting at 74° C. was obtained in insufficient quantities for analysis.

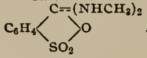
Action of Methylamine on the Unsymmetrical Chloride.—When the dry amine was passed rapidly into the solution of the unsymmetrical chloride in anhydrous ether, the temperature was soon raised to the melting-point of the chloride and the boiling-point of the ether. The ether, saturated with the methylamine vapors, carried over small quantities of the chloride, which, in contact with the air, presented a white, cloud-like appearance.

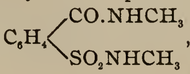
The products were treated differently, according to circumstances. When the products were viscous, the mixture was dissolved in anhydrous alcohol and attempts made to separate them by fractional crystallization. These attempts were not entirely successful, as will be shown later. However, when the reaction continued smoothly and the hydrochloride precipitated in dry, flaky condition, the entire product, after the evaporation of the ether at the ordinary laboratory temperature, was washed with ice-water in order to remove the methylamine hydrochloride. The residue is quickly pressed between layers of filter-paper and thoroughly dried. At least two compounds are formed when methylamine acts on the unsymmetrical chloride. On dissolving the dry product in warm anhydrous alcohol the methyl ester of benzoic sulphinide crystallizes out of the cold solution. The ester was also formed and in somewhat larger quantities, when the product was dissolved in dilute alcohol. The methyl benzoic sulphinide was found to be identical with that obtained from the symmetrical chloride and methylamine. The second compound of the reaction proved to be the unsymmetrical dimethylamide of orthosulphobenzoic acid.

At times as much as 15 per cent of methyl benzoic sulphinide is formed. This invariably crystallizes first, and can be separated from the syrupy mass by means of a Witt plate and a filter-pump. The unsymmetrical derivative rarely crystallized from the remaining syrup. On the other hand, it was obtained more frequently when the product from the methylamine and unsymmetrical chloride was dissolved in an excess of anhydrous ethyl alcohol at ordinary temperatures, and the solvent evaporated by passing a current of dry air over the solution, or by allowing the solution to remain in a sulphuric acid desiccator until crystallization was complete.

Infusible Dimethylamide of Orthosulphobenzoic Acid,

$C_6H_4\langle C{=}(NHCH_3)_2, SO_2 \rangle O$
, is obtained by the action of methylamine on the unsymmetrical chloride at low temperatures. It crystallizes from alcohol in plates, which are insoluble in cold water. In fact the best method of obtaining the crystals free from the mother-liquor is to wash them thoroughly with water. The amide does not fuse at 330° C. Above this temperature decomposition begins. The following analytical results were obtained for carbon and hydrogen.

0.2531 gram substance gave 0.4418 gram CO_2 and 0.1231 gram H_2O.

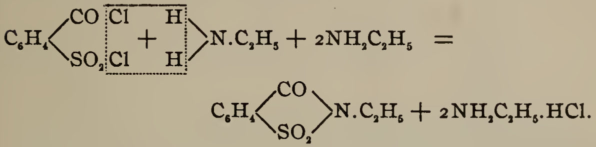
	Calculated for 	Found.
C	47.75	47.60
H	5.35	5.46

Evidently this compound is isomeric with the amide of the formula 
$C_6H_4\langle^{CO.NHCH_3}_{SO_2NHCH_3}$
, but, as has been stated, such a

compound has not been obtained except possibly in very small quantity.

It should be said that the products obtained from the action of methylamine on the unsymmetrical chloride are not easily obtained. By far the largest part of the product does not crystallize and could not be further investigated.

Action of Ethylamine on the Symmetrical Chloride of Orthosulphobenzoic Acid.—Ethyl benzoic sulphinide is the sole product of the action of anhydrous ethylamine on the symmetrical chloride in dry ethereal solution :



$$C_6H_4\left\langle\begin{matrix}CO\,\boxed{Cl & + & H} \\ SO_2\,Cl & & H\end{matrix}\right\rangle N.C_2H_5 + 2NH_2C_2H_5 =$$

$$C_6H_4\left\langle\begin{matrix}CO \\ SO_2\end{matrix}\right\rangle N.C_2H_5 + 2NH_2C_2H_5.HCl.$$

The compound was isolated by extracting the ethylamine hydrochloride from the white, pulverulent residue obtained from the ether solution with cold water and crystallizing the ethyl derivative from alcohol. It is soluble in ethyl alcohol, less so in methyl alcohol, quite soluble in acetone and benzene, slightly soluble in ligroin and warm water, and practically insoluble in cold water. Ethyl benzoic sulphinide crystallizes from dilute ethyl alcohol in acicular crystals and from anhydrous alcohol in stout prisms, melting at 94° C.

This compound has been obtained by Fahlberg and List[1] by treating sodium benzoic sulphinide with ethyl iodide at 230°, and by Brackett[2] by treating the silver salt of benzoic sulphinide with ethyl iodide. It was analyzed with the following results :

I. 0.0417 gram substance gave, by Liebig's method, 0.0503 gram $BaSO_4$.

II. 0.0964 gram substance gave, by Liebig's method, 0.1171 gram $BaSO_4$.

III. 0.1737 gram substance gave, by Liebig's method, 0.2045 gram $BaSO_4$.

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[1] Ber. d. chem. Ges., **20**, 1598.

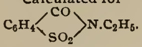
[2] This JOURNAL, **9**, 496.

IV. 0.2158 gram substance gave 0.4062 gram CO_2 and 0.0812 gram H_2O.

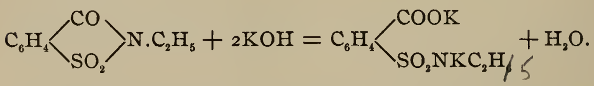
V. 0.3012 gram substance gave 0.6415 gram CO_2 and 0.1106 gram H_2O.

VI. 0.1975 gram substance gave, by the Kjeldahl method, 0.0156 gram NH_3.

VII. 0.2004 gram substance gave, by the Kjeldahl method, 0.0163 gram NH_3.

	Calculated for  $C_6H_4\langle{CO \atop SO_2}\rangle N.C_2H_5$.	Found.						
		I.	II.	III.	IV.	V.	VI.	VII.
S	16.28	16.57	16.77	16.18	....	....	....	....
C	51.31	....	....	....	51.34	51.29	....	....
H	4.25	....	....	....	4.19	4.14	....	....
N	6.63	....	....	....	....	....	6.59	6.67

Orthoethylsulphaminebenzoic Acid.—Ethyl benzoic sulphinide passes to orthoethylsulphaminebenzoic acid when hydrolyzed with alcoholic alkalies:

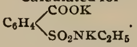


$$C_6H_4\langle{CO \atop SO_2}\rangle N.C_2H_5 + 2KOH = C_6H_4\langle{COOK \atop SO_2NKC_2H_5} + H_2O.$$

The neutral potassium orthosulphaminebenzoate crystallizes from water in very small plates, which are extremely soluble in water. Two determinations of the water of crystallization indicated 2 molecules. The anhydrous salt, when heated with sulphuric acid, yielded the following results:

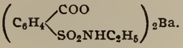
0.2005 gram substance gave 0.0992 gram K_2SO_4.

0.2851 gram substance gave 0.1415 gram K_2SO_4.

	Calculated for  $C_6H_4\langle{COOK \atop SO_2NKC_2H_5}$.	Found.	
		I.	II.
K	22.11	22.21	22.31

By heating the ethyl ester in a retort connected with a reflux condenser, for six hours, with an alcoholic solution of barium hydroxide, barium orthoethylsulphaminebenzoate was formed.

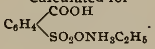
0.5102 gram substance gave 0.2020 gram $BaSO_4$.

	Calculated for  $\left(C_6H_4\left<\begin{matrix}COO\\SO_2NHC_2H_5\end{matrix}\right.\right)_2Ba$.	Found.
Ba	23.10	23.29

It is necessary to heat the ethyl ester for two days with dilute hydrochloric acid in order to transform it completely into the ethyl ammonium salt of orthosulphobenzoic acid.

The *ethyl ammonium salt* crystallizes from water in the form of delicate needles. One determination of sulphur was made.

0.2154 gram substance gave, by Liebig's method, 0.2053 gram $BaSO_4$.

	Calculated for  $C_6H_4\left<\begin{matrix}COOH\\SO_2ONH_3C_2H_5\end{matrix}\right.$.	Found.
S	12.96	13.10

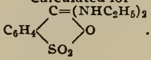
Action of Ethylamine on the Unsymmetrical Chloride.—Ethylamine, like methylamine, reacts in two ways at least with the unsymmetrical chloride. First, with the formation of the symmetrical derivative; secondly, with the formation of the infusible diethylamide of orthosulphobenzoic acid. When the product is heated with dilute alcohol, ethyl benzoic sulphinide is formed in somewhat larger quantity than in the case of methylamine and the unsymmetrical chloride. One crystallization only was necessary to bring the melting-point of the ethyl ester thus obtained to that of the product obtained from the symmetrical chloride (94° C.). There is no danger of mistaking the ester. It is perfectly characteristic in all of its reactions.

Although these reactions—of methyl- and ethylamines with the unsymmetrical chloride—are seemingly analogous in every way, there is a larger percentage of the ethyl ester formed. Experiments carried out under comparable conditions—temperature of the solutions, rate of flow of the amine, dilution of the alcohol, etc.—all confirm this statement. And, further, the ethyl ester can be removed from the reaction-products with less difficulty than in the case of the methyl ester.

The second of the products of the action of ethylamine on the unsymmetrical chloride was the infusible diethylamide of orthosulphobenzoic acid. The infusible diethylamide was obtained by evaporating slowly the alcoholic solution of the products, from which the ethylamine hydrochloride had been removed. The largest and most satisfactory crystals were obtained from an alcoholic solution, that required more than two months for the evaporation of the solvent—about 150 cc.

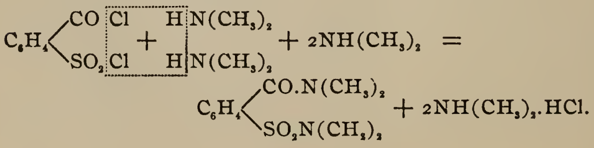
The infusible diethylamide of orthosulphobenzoic acid crystallizes in beautiful, rhombic prisms, that are insoluble in petroleum ether and chloroform; sparingly soluble in benzene and acetone; reasonably soluble in methyl and ethyl alcohols, to a less degree in the former; and insoluble in water. It yielded the following results when analyzed:

0.2754 gram substance gave 0.4991 gram CO_2 and 0.1469 gram H_2O.

	Calculated for  $C_6H_4\left\langle\begin{matrix}C{=}(NHC_2H_5)_2\\ \\ SO_2\end{matrix}\right\rangle O$	Found.
C	49.53	49.41
H	6.56	5.98

At 0° C., or slightly above this temperature, the liquid amine reacts with the unsymmetrical chloride quite satisfactorily. The product, which was colored slightly yellow, was freed from the ethylamine hydrochloride by washing it with ice-cold water. The only compound that was certainly identified was the ethyl ester of benzoic sulphinide. At —20° C. anhydrous ethylamine is entirely without action on the unsymmetrical chloride of orthosulphobenzoic acid.

Action of Diethylamine on the Symmetrical Chloride of Orthosulphobenzoic Acid.—The symmetrical chloride is quantitatively transformed into the symmetrical tetramethyldiamide of orthosulphobenzoic acid by dimethylamine in solution in anhydrous ether, according to the following reaction:



$$C_6H_4\left\langle\begin{matrix}CO\\ \\ SO_2\end{matrix}\right.\boxed{\begin{matrix}Cl & & H\\ & + & \\ Cl & & H\end{matrix}}\begin{matrix}N(CH_3)_2\\ \\ N(CH_3)_2\end{matrix} + 2NH(CH_3)_2 = C_6H_4\left\langle\begin{matrix}CO.N(CH_3)_2\\ \\ SO_2N(CH_3)_2\end{matrix}\right. + 2NH(CH_3)_2.HCl.$$

It crystallizes very well from an alcoholic solution.

The pure tetramethylorthosulphaminebenzamide yielded the following results on analysis :

I. 0.2143 gram substance gave 0.2082 gram $BaSO_4$.

II. 0.1978 gram substance gave 0.1937 gram $BaSO_4$.

III. 0.2396 gram substance gave 0.4345 gram CO_2 and 0.1424 gram H_2O.

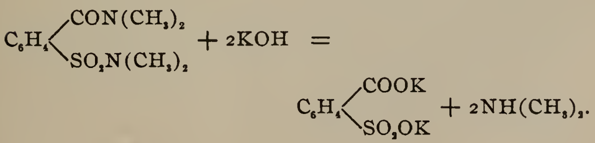
IV. 0.1851 gram substance gave 0.5162 gram CO_2 and 0.1703 gram H_2O.

V. 0.1590 gram substance gave 0.0195 gram N.

VI. 0.2508 gram substance gave 0.0285 gram N.

	Calculated for			Found.			
	$C_6H_4<\begin{matrix}CON(CH_3)_2\\SO_2N(CH_3)_2\end{matrix}$.	I.	II.	III.	IV.	V.	VI.
S	13.01	13.25	13.44	....	....	....	....
C	49.53	....	....	49.72	49.37	....	....
H	6.56	....	....	6.66	6.67	....	....
N	11.37	....	....	....	....	12.26	11.38

Unlike the esters of benzoic sulphinide, tetramethylorthosulphaminebenzamide is not changed by alcoholic caustic alkalies. Like the esters, it is not decomposed by dilute aqueous caustic alkalies. Concentrated aqueous alkalies give the corresponding salt of orthosulphobenzoic acid and dimethylamine :



$$C_6H_4<\begin{matrix}CON(CH_3)_2\\SO_2N(CH_3)_2\end{matrix} + 2KOH = C_6H_4<\begin{matrix}COOK\\SO_2OK\end{matrix} + 2NH(CH_3)_2.$$

Dilute mineral acids do not hydrolyze the compound.

A crystallographic examination[1] gave the following results :

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[1] The crystallographic work herein described was done by Dr. E. B. Matthews and Mr. A. Johannsen.

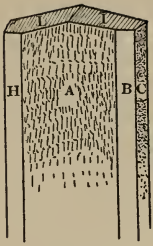


Fig. I.

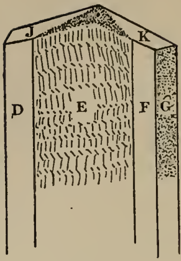


Fig. II.

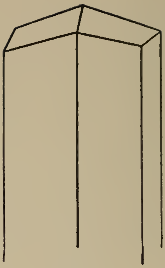


Fig. III.

The crystals were found to be of two habits, both tabular, parallel to the front pinacoid (100), but differing in the presence or absence of the front pinacoid. The crystals are simple and show but few faces. Figs. I. and II. are front and back views of the same crystal, and Fig. III. is of the other type.

Faces *A* and *E* were imperfect, showing many small cavities or incomplete growth. Faces *L* and *I*, which were striated parallel to the edge *LI*, were large and extended almost entirely across the crystals, giving them a monoclinic appearance. The edges *IB* and *LH* were so imperfect that they could not be used in measurements. Faces *J* and *K* were very small and their edges against the pinacoidal were indistinct, rendering measurements of these angles impossible.

The average of the angles observed were as follows :

HA, AB, DE, DF,	12° 30′.	Range of reading, 9′.
BC, CD, FG, GH,	77° 30′.	Range of reading, 17′.
BH, FD,	25° 00′.	
IJ,	60° 35′.	
JD,	44° 12′.	
CI,	73° 25′.	
IA, LA,	70° 21′.	
LI,	32° 10′.	

JE, KE, IB, and LA were indeterminate.

The foregoing measurements did not clearly prove the monoclinic or orthorhombic character of the crystals, but optical tests showed parallel extinction with the emergence of a bisectrix in section parallel to *A*. The extinction shown when the crystal was examined parallel to *C* was also parallel. The plane of the optic axes was perpendicular to the tabular face. From the parallel extinction in two directions it is concluded that the crystals are orthorhombic, though the conclusion is neither proved nor disproved by the crystal measurements. On the assumption that the crystals are orthorhombic, the following crystallographic constants are found:

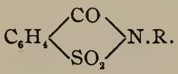
Axial ratio $a : b : c$. 0.232 : 1 : 0.127.

Action of Dimethylamine on the Unsymmetrical Chloride.—The only product of the action of dimethylamine on the unsymmetrical chloride that was isolated was the compound obtained from the symmetrical chloride and dimethylamine. No infusible product, corresponding to the primary amine derivative, was isolated.

Summary.

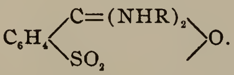
This investigation has shown:

1. That the symmetrical chloride reacts with primary amines with the formation of the esters of benzoic sulphinide of the general formula,



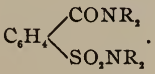
$$C_6H_4\left\langle\begin{matrix}CO\\SO_2\end{matrix}\right\rangle N.R.$$

2. That the unsymmetrical chloride with primary amines yields small amounts of the esters of benzoic sulphinide, together with infusible disubstituted amides:



$$C_6H_4\left\langle\begin{matrix}C{=}(NHR)_2\\SO_2\end{matrix}\right\rangle O.$$

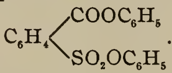
3. That the secondary amines react normally with the symmetrical chloride, giving rise to compounds of the general formula,

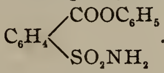
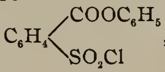


$$C_6H_4\left\langle\begin{matrix}CONR_2\\SO_2NR_2\end{matrix}\right. .$$

IV. THE ACTION OF PHENOL ON THE CHLORIDES OF ORTHOSULPHOBENZOIC ACID.[1]

BY ROBERT E. HUMPHREYS.

In the year 1894, Remsen and Saunders[2] studied the action of phenol on what were then known as the solid and liquid chlorides of orthosulphobenzoic acid. When phenol was added to the mixed chlorides they passed into solution, but no reaction was observed to take place in the cold. On warming, the evolution of hydrochloric acid began at once, and the liquid assumed a clear, lake-red color, which became more intense as the reaction proceeded. When poured into a hot solution of dilute sodium hydroxide, a crystalline product separated which proved to be the diphenyl ester of orthosulphobenzoic acid,  $C_6H_4\left\langle\begin{matrix}COOC_6H_5\\SO_2OC_6H_5\end{matrix}\right.$. When the solid chloride alone was employed, the same products were formed as with a mixture of the chlorides. The liquid chloride, when treated in the same way, showed the usual color reaction, and when the product was poured into dilute sodium hydroxide a heavy, yellow oil settled to the bottom of the vessel and became crystalline after a time. On recrystallizing this from alcohol two substances were isolated. One of these crystallized in needles and proved to be the diphenyl ester of orthosulphobenzoic acid, and the other crystallized in clear, thin columns, which melted at 98° to 100°. The latter product was not studied. The coloring-matter was supposed to be phenolsulphonephthaleïn.

In the following year Remsen and McKee[3] repeated this work. They obtained the diphenyl ester of orthosulphobenzoic acid without difficulty, but made no mention of finding the substance which melted at 98° to 100°. They tried the effect of treating the reaction-products with dilute ammonia instead of dilute sodium hydroxide. In this case the whole mass became oily, but solidified when allowed to stand for some time. This, when crystallized from alcohol, yielded the diphenyl ester of orthosulphobenzoic acid, and a new substance which was called phenyl orthosulphaminebenzoate and given the formula  $C_6H_4{<}^{COOC_6H_5}_{SO_2NH_2}$. They described the crystals as feathery-shaped, and gave the melting-point as 131° to 132°. They were not able to isolate the substance that formed this amide with ammonia, but supposed it to be the orthosulphone chloride of phenyl benzoate,  $C_6H_4{<}^{COOC_6H_5}_{SO_2Cl}$, formed according to the following equation:

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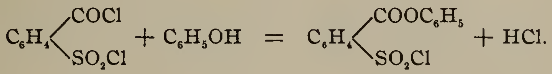
[1] From the author's dissertation submitted, June, 1900, to the Board of University Studies of the Johns Hopkins University in conformity with the requirements for the degree of Doctor of Philosophy.

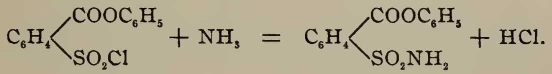
[2] This JOURNAL, **17**, 352.

[3] *Ibid.*, **18**, 794.



$$C_6H_4{<}^{COCl}_{SO_2Cl} + C_6H_5OH = C_6H_4{<}^{COOC_6H_5}_{SO_2Cl} + HCl.$$

This, they thought, reacted with ammonia to form phenyl orthosulphaminebenzoate in the following manner:



$$C_6H_4{<}^{COOC_6H_5}_{SO_2Cl} + NH_3 = C_6H_4{<}^{COOC_6H_5}_{SO_2NH_2} + HCl.$$

In an article by List and Stein[1] on the chlorides of orthosulphobenzoic acid, the authors make the following statement with reference to this phenyl orthosulphaminebenzoate obtained by Remsen and McKee:

"On the contrary, in spite of the most careful experiments, we have in vain attempted to obtain the phenyl ester of orthosulphaminebenzoic acid. According to our experiments, the ester does not seem to be capable of existence. We did not obtain it either by treating the reaction-product of phenol and the chloride with aqueous ammonia, or by bringing together the pure phenyl ester chloride with ammonia water."

In consequence of this statement, Prof. Remsen suggested the advisability of repeating the work of McKee and of making a careful investigation of phenylorthosulphaminebenzoate

[1] Ber. d. chem. Ges., 31, 1648.

and the orthosulphone chloride of phenyl benzoate. The results of this investigation are recorded in this paper.

Confirmation of the Work of Remsen and McKee.—Two and a half grams of the symmetrical chloride were heated with 2 grams (2 molecules) of phenol in a test-tube for five hours at 40° to 45°. The reaction proceeded very slowly and was accompanied by the formation of a red coloring-matter, phenolsulphonphthaleïn.[1] The reaction-products, while hot, were poured into a small mortar containing ordinary, dilute ammonia, and stirred with a pestle. The mass formed a thick, viscous liquid, which required at least an hour, and frequently, in repetition of this experiment, four to five hours to solidify. The hardened product was finely triturated, washed, dried, and dissolved in 30 cc. of 96 per cent alcohol. On cooling, the diphenyl ester of orthosulphobenzoic acid separated in fine needles. These were filtered off and the filtrate evaporated down to a volume of 6 cc. On standing, small, heavy, transparent crystals formed which melted at 130° to 131°, and after recrystallization at 131° to 132°. This product corresponded in every way to the phenyl orthosulphaminebenzoate described by Remsen and McKee.

The above experiment was varied in many ways, but the general results were always the same. If the reaction-products were allowed to cool and then poured into cold, dilute ammonia and washed with cold water the yield of phenyl orthosulphaminebenzoate was increased, but if treated with warm ammonia and washed with hot water it was considerably lessened. Working under the best conditions, 3 grams of diphenyl ester and 1 gram of phenyl orthosulphaminebenzoate were obtained from 5 grams of the symmetrical chloride.

Two and one-half grams of unsymmetrical chloride were heated with 2 grams of phenol for five hours at 40° to 45°. The reaction was more rapid than in the case of the symmetrical chloride, but in general it appeared to proceed in the same way. The mass was poured into dilute ammonia and then treated exactly as above. The diphenyl ester separated out of the solution in alcohol. The filtrate from this was concentrated and allowed to stand. None of the phenyl orthosulphaminebenzoate appeared. When the solution was brought almost to dryness a small quantity of oil separated which had a strong odor of phenol. No success ever attended the efforts to get phenyl orthosulphaminebenzoate by this process. The substance obtained from the symmetrical chloride gave the following analytical results:

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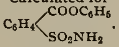
[1] Remsen and Sohon: This JOURNAL, 20, 263.

I. 0.2973 gram substance gave 0.6098 gram CO_2 and 0.1075 gram H_2O.

II. 0.1678 gram substance gave 0.3455 gram CO_2 and 0.0625 gram H_2O.

III. 0.2428 gram substance gave 0.2028 gram $BaSO_4$.

IV. 0.5773 gram substance required 15 cc. standard sulphuric acid (1 cc. = 0.00256 gram N), less 2 cc. standard soda (1 cc. = 0.004125 gram N), Kjeldahl method.

	Calculated for	Found.	
	 $C_6H_4\left<\begin{matrix}COOC_6H_5\\SO_2NH_2\end{matrix}\right.$.	I.	II.
C	56.28	55.90	56.15
H	3.99	4.04	4.16
N	5.07	5.08	....
S	11.57	11.57	....

Formation of Phenyl Orthosulphaminebenzoate.—Remsen and McKee[1] did not isolate the substance that reacted with ammonia to form phenyl orthosulphaminebenzoate. A careful search was, therefore, made for it. The best yield was obtained when the symmetrical chloride and phenol were heated at 40° to 45°, and this was the temperature employed in the following experiments.

Two and one-half grams of the symmetrical chloride were mixed with 2 grams of phenol and heated for five hours at the temperature mentioned above. The mass was poured into a small mortar and rubbed up first with cold water and afterwards with boiling water. Most of the coloring-matter was thus removed. After solidification it was finely triturated, filtered off, dried, and dissolved in glacial acetic acid. By fractional crystallization three substances were isolated which melted at 118° to 119°, 103° to 104°, and 79°.5, respectively. The first proved to be the diphenyl ester of orthosulphobenzoic acid, the second the orthosulphone chloride of phenyl benzoate, and the third an unchanged portion of the symmetrical chloride. The orthosulphone chloride of phenyl benzoate was treated in the cold with aqueous ammonia, but there was no evidence of the formation of phenyl orthosulphaminebenzoate.

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[1] *Loc. cit.*

Another portion of the symmetrical chloride was heated with phenol, as above, and the product washed with cold water only. On crystallizing from glacial acetic acid the same products were obtained as in the preceding experiment. Again, the reaction-products were poured, without washing, directly into glacial acetic acid. After twelve hours a mass of crystals separated, but there was no evidence of the presence of any substance except those mentioned above. The crystals were filtered off and the filtrate poured into water. An oily substance separated, which was extracted with ether, dried over calcium chloride, and allowed to stand. After some time a few crystals of the diphenyl ester appeared, but nothing else was ever obtained. This part of the work was rendered very difficult by the presence of red coloring-matter.

Thinking that perhaps both hot and cold water destroyed the substance that formed phenyl orthosulphaminebenzoate on treatment with ammonia, the products were poured into absolute ether and allowed to crystallize. The beaker containing the solution was kept in a desiccator; crystals formed slowly and were removed from time to time and carefully examined. This was continued until the solution evaporated completely. No substances other than those already mentioned were discovered.

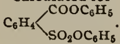
It became clear that the phenyl orthosulphaminebenzoate must have been formed by the action of ammonia upon the symmetrical chloride that escaped reaction with phenol. The reaction between the chloride and phenol was never complete, even when the heating at 40° to 45° was continued for five hours. Occasionally, when the mass was not frequently stirred during the heating, considerable of the chloride remained unacted upon. It was possible that ammonia, in the presence of phenol, would react upon this to form phenyl orthosulphaminebenzoate.

Two grams of phenol were dissolved in 25 cc. of dilute ammonia and to this 2.5 grams of symmetrical chloride were added. Reaction began at once. The chloride was converted into a thick oil, which settled to the bottom of the vessel, and the solution became quite warm. After stirring for some time the oil solidified. This was filtered off, dried, and crystallized from alcohol. A mass of fine needles separated out which melted at 118° and appeared to be the diphenyl ester of orthosulphobenzoic acid, and so proved to be when it was recrystallized and submitted to analysis. When the filtrate was evaporated somewhat, it yielded a crop of clear, thick crystals, which, on purification, melted at 131° to 132°, and were exactly similar in all respects to those obtained by former methods.

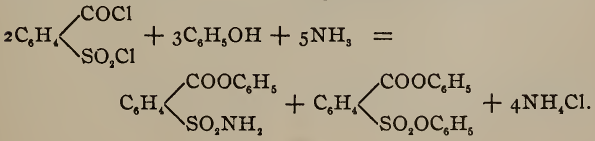
The analysis of the needles gave the following results:

I. 0.1582 gram substance gave 0.3722 gram CO_2 and 0.0631 gram H_2O.

II. 0.1919 gram substance gave 0.4519 gram CO_2 and 0.0712 gram H_2O.

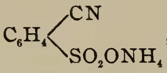
	Calculated for	Found.	
	 $C_6H_4\left\langle\begin{matrix}COOC_6H_5\\SO_2OC_6H_5\end{matrix}\right.$.	I.	II.
C	64.37	64.16	64.21
H	3.98	4.46	4.13
S	9.05	8.65	....

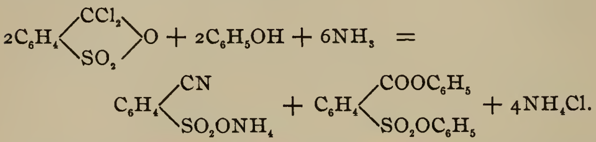
The above reaction was brought about in various ways. The chloride was dissolved in phenol and dilute ammonia slowly added with stirring. In some cases the mixture was allowed to get hot, in others it was cooled with tap-water or with ice-water. Phenyl orthosulphaminebenzoate was always formed, but the best yield was obtained when the chloride was dissolved in phenol and ammonia added in only slight excess. The following equation expresses the reaction:



$$2C_6H_4\left\langle\begin{matrix}COCl\\SO_2Cl\end{matrix}\right. + 3C_6H_5OH + 5NH_3 =$$

$$C_6H_4\left\langle\begin{matrix}COOC_6H_5\\SO_2NH_2\end{matrix}\right. + C_6H_4\left\langle\begin{matrix}COOC_6H_5\\SO_2OC_6H_5\end{matrix}\right. + 4NH_4Cl.$$

Two grams of unsymmetrical chloride were treated as above with phenol and ammonia. The oily mass at first formed was stirred until it solidified. It was then filtered off and crystallized from alcohol. Needles of the diphenyl ester separated. When the filtrate was evaporated from the needles no phenyl orthosulphaminebenzoate was obtained. The unsymmetrical chloride could not be induced to yield this product, although the experiments were carried out under many conditions of temperature, and with variations of the order of mixing the ingredients. The unsymmetrical chloride is partly converted into the ammonium salt of orthocyanbenzenesulphonic acid,  $C_6H_4\left\langle\begin{matrix}CN\\SO_2ONH_4\end{matrix}\right.$, and partly into the diphenyl ester of orthosulphobenzoic acid :



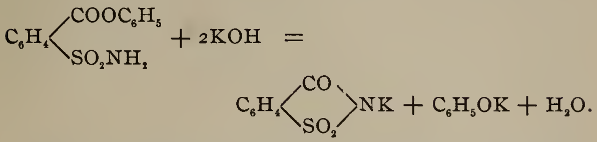
$$2C_6H_4\left\langle\begin{matrix}CCl_2\\SO_2\end{matrix}\right\rangle O + 2C_6H_5OH + 6NH_3 = C_6H_4\left\langle\begin{matrix}CN\\SO_2ONH_4\end{matrix}\right. + C_6H_4\left\langle\begin{matrix}COOC_6H_5\\SO_2OC_6H_5\end{matrix}\right. + 4NH_4Cl.$$

Properties of Phenyl Orthosulphaminebenzoate.—The melting-point is 132°. It is easily soluble in alcohol, acetone, and glacial acetic acid ; moderately soluble in benzene ; and difficultly soluble in ether, ligroin, hot water, and hot, dilute hydrochloric acid. The crystals are triclinic showing base, right and left prisms, and, occasionally, left negative pyramid, left brachydome, and macro-pinacoid. β is approximately 27°, α approximately 113°. γ was not determined. The basal cleavage is medium good, and luster vitreous. Medium index of refraction and low double refraction. Extinction $+ 5° 15'$ off the right prismatic face on basal section.

Dilute potassium hydroxide readily converts it into the potassium salt of benzoic sulphinide.

Dilute ammonia acts in the same way. It is also slowly hydrolyzed by boiling water. It is soluble in hot water to an extent that permits of its purification by this means. The diphenyl ester of orthosulphobenzoic acid, the substance most commonly contaminating it, is thus easily removed, as it is insoluble in hot water.

It is probable that the reaction proceeds according to the following equation:



$$C_6H_4\left\langle\begin{matrix}COOC_6H_5\\SO_2NH_2\end{matrix}\right. + 2KOH = C_6H_4\left\langle\begin{matrix}CO\\SO_2\end{matrix}\right\rangle NK + C_6H_5OK + H_2O.$$

Cresyl Orthosulphaminebenzoates.—It seemed desirable to try the action of the cresols on the chlorides of orthosulphobenzoic acid in the presence of ammonia in order to see if it is analogous to that of phenol. This was found to be the case. Only the ortho- and paracresols were employed. They reacted with more difficulty than phenol, and this was especially true of orthocresol. Both of the cresyl orthosulphaminebenzoates were prepared from the symmetrical chloride. The unsymmetrical chloride does not react with the cresols.

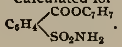
Orthocresyl Orthosulphaminebenzoate.–Two and one-half grams of symmetrical chloride are placed in a beaker with 1 gram of orthocresol and an excess of dilute ammonia. The whole is heated on the water-bath and vigorously stirred until the oily mass solidifies. This requires about ten minutes. The product must remain solid when heated up nearly to 100°. The chloride is thus converted into orthocresyl orthosulphaminebenzoate, and the dicresyl ester of orthosulphobenzoic acid, the former largely predominating. It is purified by recrystallization from alcohol. Its melting-point is 152°. On analysis the following results were obtained:

I. 0.1753 gram substance gave 0.1395 gram $BaSO_4$.

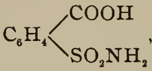
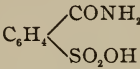
II. 0.1701 gram substance gave 0.1470 gram $BaSO_4$.

III. 0.3600 gram substance gave, by the Kjeldahl method, 0.0122 gram N.

IV. 0.3954 gram substance gave 0.01854 gram N.

	Calculated for  $C_6H_4\left\langle\begin{matrix}COOC_7H_7\\SO_2NH_2\end{matrix}\right.$.	Found.	
		I.	II.
S	11.01	10.92	11.58
N	4.82	4.78	4.69

Paracresyl Orthosulphaminebenzoate.—This is made by the method above mentioned. Paracresol reacts more easily than orthocresol, and the proportion of the dicresyl ester formed was much greater than in the preceding experiment.

It is impossible to say positively from a consideration of the foregoing reactions whether the amido group is in the benzoic acid or the sulphonic acid group, though they make it probable that it is the latter. In order to settle this question the following line of investigation was taken up. Orthosulphaminebenzoic acid,  $C_6H_4\begin{cases}COOH\\SO_2NH_2\end{cases}$, and orthocarbaminesulphonic acid,  $C_6H_4\begin{cases}CONH_2\\SO_2OH\end{cases}$, are both known, having been carefully investigated in this laboratory by F. D. Wilson.[1] It was proposed to make the phenyl esters of each of these acids and compare them with the phenyl orthosulphaminebenzoate, so-called, made by the action of phenol and ammonia on the symmetrical chloride.

Phenyl Orthocarbaminesulphonate. —– Orthocarbaminesulphonic acid was made according to the method given by Wilson. This was converted into the chloride by heating the potassium salt with phosphorus oxychloride. The chloride is placed in a beaker with a little more than the calculated quantity of phenol and a slight excess of a dilute solution of potassium hydroxide. The whole is heated on a water-bath and stirred until the oily mass solidifies. It is then filtered off, carefully washed, and crystallized from alcohol. The crystals separate in the form of plates or needles. They are colorless and the melting-point is 95°. The product obtained as above gave the following analytical results :

I. 0.1502 gram substance gave 0.1322 gram $BaSO_4$.

II. 0.1231 gram substance gave 0.1059 gram $BaSO_4$.

III. 0.3866 gram substance gave, by the Kjeldahl method, 0.0206 gram N.

IV. 0.4098 gram substance gave 0.0216 gram N.

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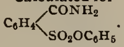
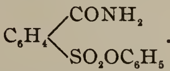
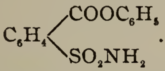
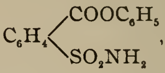
[1] Dissertation, 1899.

	Calculated for  $C_6H_4\begin{matrix}\diagup CONH_2\\ \diagdown SO_2OC_6H_5\end{matrix}$.	Found. I.	II.
S	11.57	12.11	11.81
N	5.07	5.32	5.27

The method of formation clearly indicates that the correct formula of this substance is  $C_6H_4\begin{matrix}\diagup CONH_2\\ \diagdown SO_2OC_6H_5\end{matrix}$. It is entirely different from the substance obtained from the symmetrical chloride by treating with phenol and ammonia. Its melting-point is 37° lower, and its mode of crystallization quite different. Toward most of the reagents that easily act upon the phenyl orthosulphaminebenzoate it is stable. It resists the action of hot, dilute potassium hydroxide to a far greater degree, and is not converted by it into a salt of benzoic sulphinide.

Phenyl Orthosulphaminebenzoate.—The attempt was next made to prepare the phenyl ester of orthosulphaminebenzoic acid,  $C_6H_4\begin{matrix}\diagup COOC_6H_5\\ \diagdown SO_2NH_2\end{matrix}$. The acid was prepared according to directions given by Wilson.[1] Wilson was not able to make the chloride of this acid, and our attempts were also unsuccessful. Thinking that the ester might be made by direct treatment of the acid or its salts, various methods were tried. The acid was warmed with phenol and phosphorus oxychloride gradually added. A vigorous reaction resulted, but no ester was formed. The acid was transformed into benzoic sulphinide. When phosphorus pentachloride was employed instead of the oxychloride the result was the same. Then a mixture of the acid (1 part), phenol (4 parts), and concentrated sulphuric acid (0.2 part) was heated on the water-bath for eight hours. At intervals of one hour small portions were removed and examined for the ester. It was found that the formation of benzoic sulphinide began immediately and continued slowly to complete reaction. No evidence of the formation of the ester was found. The silver salt of the acid was prepared and heated with phenyl iodide at 125° for three days. As far as could be discovered, little or no reaction had occurred. Further efforts to prepare this ester were abandoned for lack of time. While it was not possible to prepare and compare it with the one formed by treatment of the symmetrical chloride with phenol and ammonia, yet the formula previously assigned to the latter substance,  $C_6H_4\begin{cases}COOC_6H_5\\SO_2NH_2\end{cases}$, is rendered very probable by the fact that the phenyl ester of orthocarbaminesulphonic acid was shown to be quite a different substance. Other considerations pointing to the correctness of this view will be taken up in the general discussion of results.

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[1] *Loc. cit.*

Orthosulphone Chloride of Phenylbenzoate.—This substance is formed from both chlorides by heating them with phenol. In order to determine its proportion relative to that of the diphenyl ester of orthosulphobenzoic acid formed at the same time, the following experiments were undertaken: Two and one-half grams of each chloride were placed in a test-tube with 2 grams of phenol and heated five hours in a sulphuric acid-bath. A series of six experiments was made with each chloride at each of the following temperatures: 40° to 45°, 65° to 70°, 100°, and 135°.

At 40° to 45°, the lowest temperature at which reaction appeared to take place, the reaction proceeded very slowly and was never complete with either chloride at the end of five hours. The red mass formed was poured into a mortar and rubbed successively with cold and with hot water until the coloring-matter was removed as far as possible. This could not be completely effected, even by washing with dilute alkali. When poured into water the reaction-products form an oil which, as the washing proceeds, passes through a viscous stage to the solid state. This was then finally triturated, filtered off, and dried. The product from the symmetrical chloride had a pale-yellow color, and that from the unsymmetrical was nearly white. These were crystallized from glacial acetic acid. From the symmetrical chloride the diphenyl ester of orthosulphobenzoic acid, and the orthosulphone chloride of phenyl benzoate were formed, the former in much greater quantity than the latter. The diphenyl ester crystallizes in needles, and the orthosulphone chloride of phenyl benzoate in heavy prisms. These could be roughly separated by the method of subsidence, but only an approximate determination could be made of the relative quantities present.

From the unsymmetrical chloride, the orthosulphone chloride of phenyl benzoate was formed almost exclusively, only a few needles of the diphenyl ester appearing.

At 60° to 65° the reaction-products were more highly colored and more difficult to wash free of coloring-matter. Some color remained even after most vigorous methods were used to remove it. When poured into a mortar and water added, each solidified at once without passing through the oily-viscous stages. The washed product from the symmetrical chloride had a light-yellow color, while that from the unsymmetrical was pink. The same products were formed as at the lower temperature, but in somewhat different proportions. From the symmetrical chloride the diphenyl ester was formed in larger quantity, the phenyl ester chloride in smaller. The same was found to be true in the case of the unsymmetrical chloride.

At 100° the products from the symmetrical chloride were a very small quantity of phenyl ester chloride and a relatively larger quantity of diphenyl ester. From the unsymmetrical, these two products were formed in about equal proportions.

At 130° the product from each chloride consisted wholly of diphenyl ester.

Taking these facts into consideration, the best method of preparing the orthosulphone chloride of phenyl benzoate is as follows :

One molecule of unsymmetrical chloride is heated with 2 molecules of phenol from twelve to sixteen hours at 40° to 45°. The mass is washed thoroughly with hot water, allowed to solidify, and crystallized from glacial acetic acid. The crystals are large and colorless and melt at 103° to 104°. When crystallized from alcohol they have the appearance of rhombs. It is easily soluble in alcohol and glacial acetic acid, and difficultly soluble in ether and benzene. The substance prepared as above, gave the following results on analysis :

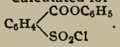
I. 0.1868 gram substance gave 0.3600 gram CO_2 and 0.0611 gram H_2O.

II. 0.2257 gram substance gave 0.4386 gram CO_2 and 0.0666 gram H_2O.

III. 0.1845 gram substance gave 0.3522 gram CO_2 and 0.520 gram H_2O.

IV. 0.1522 gram substance gave 0.1175 gram $BaSO_4$ and 0.0761 gram AgCl.

V. 0.1426 gram substance gave 0.1101 gram $BaSO_4$ and 0.0714 gram AgCl.

	Calculated for		Found.	
	 $C_6H_4\langle{}^{COOC_6H_5}_{SO_2Cl}$.	I.	II.	III.
C	52.62	52.56	52.99	52.06
H	3.04	3.63	3.29	3.14
S	10.79	10.64	10.59	....
Cl	11.97	11.68	12.37	....

Action of Acids, Water, Alkalies, Etc., upon the Phenyl Ester Chloride.

Dilute hydrochloric and *sulphuric acids* readily saponify the ester chloride when boiled with it, giving *o*-sulphobenzoic acid.

Water causes about the same decomposition when boiled with it for six hours.

The phenyl ester chloride was boiled with a solution of barium hydroxide which was saturated at the ordinary temperature. After two hours the thick, oily drops floating about in the solution solidified in a crystalline condition, and further boiling produced no change. The solid was filtered off, washed, and crystallized from alcohol. Fine needles separated which melted at 118° and had the well-known appearance of the diphenyl ester of orthosulphobenzoic acid. The filtrate yielded crystals of barium orthosulphobenzoate.

I. 0.1875 gram substance gave 0.1171 gram $BaSO_4$.

II. 0.1946 gram substance gave 0.1210 gram $BaSO_4$.

	Calculated for $C_7H_4SO_5 + 2H_2O$.	Found.	
		I.	II.
Ba	36.79	36.76	36.59

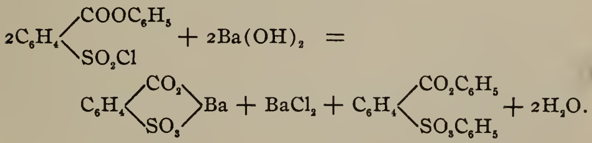
The needles gave the following analytical results for carbon and hydrogen:

I. 0.1752 gram substance gave 0.4115 gram CO_2 and 0.0635 gram H_2O.

II. 0.1973 gram substance gave 0.4600 gram CO_2 and 0.0704 gram H_2O.

	Calculated for $C_6H_4\begin{matrix}COOC_6H_5\\SO_2OC_6H_5\end{matrix}$.	Found.	
		I.	II.
C	64.39	64.06	64.05
H	3.98	4.03	3.96

The formation of the diphenyl ester under these conditions was unexpected, although it is easily explained as a special form of the Schotten-Baumann reaction:



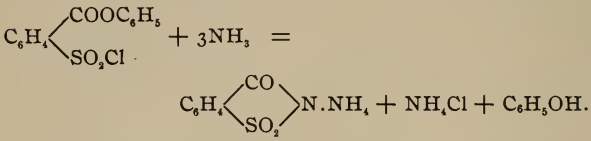
$$2C_6H_4\begin{matrix}COOC_6H_5\\SO_2Cl\end{matrix} + 2Ba(OH)_2 =$$
$$C_6H_4\begin{matrix}CO_2\\SO_3\end{matrix}Ba + BaCl_2 + C_6H_4\begin{matrix}CO_2C_6H_5\\SO_3C_6H_5\end{matrix} + 2H_2O.$$

A similar experiment was carried out with a solution of potassium hydroxide. There was a gradual formation of the diphenyl ester, which continued for two hours, when the reaction was complete. The other product of the reaction was orthosulphobenzoic acid. No constant quantitative relations between these products were discovered in this or the preceding experiment.

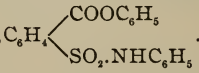
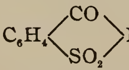
Aqueous *ammonia* acts only slightly on the orthosulphone chloride of phenyl benzoate in the cold, but when the temperature is raised the reaction proceeds very smoothly with the formation of the ammonium salt of benzoic sulphinide.

One gram of the substance was dissolved in absolute ether and the solution placed in a small cylinder, which was kept cool with ice-water. Dry ammonia gas was slowly passed through this for an hour. A white precipitate gradually formed, and this was filtered off and dried. When dissolved in a small amount of water, this gave a precipitate of benzoic sulphinide on the addition of strong hydrochloric acid.

The above experiment was repeated and the ether kept at a temperature of 30°. The reaction took place essentially as before. The phenyl ester chloride in solution in ether is decomposed by ammonia according to the following equation:



$$C_6H_4\left\langle\begin{array}{l}COOC_6H_5\\ SO_2Cl\end{array}\right. + 3NH_3 = C_6H_4\left\langle\begin{array}{c}CO\\ SO_2\end{array}\right\rangle N.NH_4 + NH_4Cl + C_6H_5OH.$$

Action of Aniline.—It was thought that aniline would react with the orthosulphone chloride of phenyl benzoate to form the orthosulphone anilide of phenyl benzoate,  $C_6H_4\left\langle\begin{array}{l}COOC_6H_5\\ SO_2.NHC_6H_5\end{array}\right.$. Finely powdered orthosulphone chloride of phenyl benzoate was added to an emulsion of aniline in water. An oily mass was formed which slowly solidified. The solid was freed from aniline by washing, first with dilute hydrochloric acid and then water. On crystallizing from glacial acetic acid, unchanged phenyl ester chloride first separated, and afterwards a small quantity of long, white blades which melted at 190° to 191°. They were insoluble in water and alkalies, and proved to be the anil,  $C_6H_4\left\langle\begin{array}{c}CO\\ SO_2\end{array}\right\rangle N.C_6H_5$, described by Remsen and Coates.[1] When the substance was treated with pure aniline, the yield of the anil was quite good. No evidence of the formation of the orthosulphone anilide of phenyl benzoate was observed. Finally, some phenyl ester chloride was dissolved in ether, and to this was added a solution of aniline in ether. The reaction was very slow. Only the anil in small quantity was formed.

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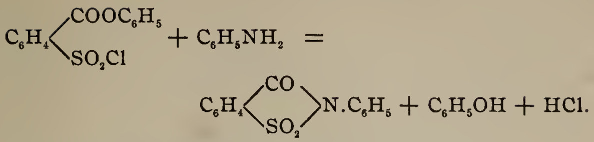
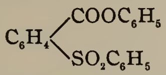
[1] This Journal, 17, 311.



$$C_6H_4\left\langle\begin{matrix}COOC_6H_5\\SO_2Cl\end{matrix}\right. + C_6H_5NH_2 = C_6H_4\left\langle\begin{matrix}CO\\SO_2\end{matrix}\right\rangle N.C_6H_5 + C_6H_5OH + HCl.$$

An attempt was made to prepare the compound



$$C_6H_4\left\langle\begin{matrix}COOC_6H_5\\SO_2C_6H_5\end{matrix}\right.$$

from the ester chloride by means of the reaction of Friedel and Crafts, but the attempt was unsuccessful.

Five grams of the substance were placed in a small flask connected with an inverted condenser and boiled with absolute alcohol for twelve hours. The alcohol was distilled off and the residue heated on the water-bath to expel the last traces of hydrochloric acid. This residue had a strong odor of phenol. A small quantity of water was added and the solution neutralized with barium carbonate. The filtrate from the excess of the carbonate was evaporated to a small volume and a few cubic centimeters of alcohol added. On standing, very fine needles separated out. These were filtered off, washed with alcohol, and dried. Analysis gave the following results:

I. 0.3906 gram substance lost 0.0044 gram when heated to 150°.

II. 0.1035 gram substance gave 0.0500 gram $BaSO_4$.

III. 0.3239 gram substance gave 0.1557 gram $BaSO_4$.

IV. 0.2437 gram substance gave 0.1171 gram $BaSO_4$.

		Found.	
Calculated for	I.	II.	III.
Ba	28.42	28.29	28.28

This substance was not fully identified and needs further investigation.

Action of Phenol in the Presence of Dilute Potassium Hydroxide.—As was mentioned in a previous part of this paper, when the attempt is made to saponify the orthosulphone chloride of phenyl benzoate with alkalies, the reaction is always accompanied by the formation of diphenyl ester of orthosulphobenzoic acid. This suggested the following experiments:

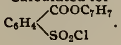
One gram of the orthosulphone chloride of phenyl benzoate was boiled with an excess of phenol and dilute potassium hydroxide. In a short time the oily mass first formed solidified. This was filtered off and crystallized from alcohol. Needles of the diphenyl ester separated and this was the sole product. The reaction was smooth and rapid.

One gram each of the symmetrical and unsymmetrical chlorides were treated with phenol and the smallest possible excess of dilute potassium hydroxide in the cold. The viscous masses first formed were stirred until they solidified. On crystallization from glacial acetic acid it was found that nothing but the diphenyl ester was formed from the symmetrical chloride, but both diphenyl ester and the orthosulphone chloride of phenyl benzoate were formed from the unsymmetrical, the latter in larger quantity than the former. When care is taken to keep the temperature low, the phenyl ester chloride can be obtained in nearly pure condition by means of this reaction. It is a convenient and rapid method for preparing all the members of this class of compounds. When the method of heating the chlorides with phenol is employed the process is long and coloring-matters are formed at the same time that are extremely difficult to remove. All this is avoided by the method just described.

When the temperature is allowed to rise during this reaction the diphenyl ester alone is formed.

Action of the Cresols on the Chlorides of Orthosulphobenzoic Acid.—One gram each of the symmetrical and unsymmetrical chlorides were heated with 1 gram of orthocresol at 60° to 65° for two days. This was the lowest temperature at which a fairly good reaction would take place. Even at this temperature it was necessary to heat for two days to obtain a good yield. Coloring-matter was formed in large quantity with each chloride and was very hard to remove. The solid product was crystallized from glacial acetic acid. From the symmetrical chloride nothing definite could be isolated. From the unsymmetrical the orthosulphone chloride of orthocresyl benzoate was obtained. This crystallizes in rhomb-like forms and melts at 112°. The substance was analyzed with the following results:

I. 0.2513 gram substance gave 0.1133 gram AgCl.
II. 0.2360 gram substance gave 0.1112 gram AgCl.
III. 0.2994 gram substance gave 0.2281 gram $BaSO_4$.

	Calculated for  $C_6H_4\begin{cases}COOC_7H_7\\SO_2Cl\end{cases}$.	Found.	
		I.	II.
Cl	11.41	11.15	11.64
S	10.32	10.46	....

When the chlorides were treated with orthocresol and dilute potassium hydroxide the unsymmetrical goes over easily into the orthosulphone chloride of orthocresyl benzoate. The symmetrical is decomposed by the alkali without the formation of this substance or the diorthocresyl ester to any considerable extent. Only a few crystals of the latter were obtained. These had the form of needles, resembling somewhat the crystals of the diphenyl ester (m. p. 141°). The difficulty encountered in the formation of this ester must be due to the protective influence of the group in the ortho position. The diphenyl ester is formed with the greatest ease by this method, and the diparacresyl ester is also obtained without trouble.

The orthosulphone chloride of paracresyl benzoate is obtained by heating the unsymmetrical chloride with paracresol, or by treating it with paracresol and dilute potassium hydroxide. Some diparacresyl ester is obtained at the same time if the temperature in either case is high. The symmetrical chloride, under the same treatment, yields diparacresyl ester.

ON RELATIONS BETWEEN THE COLOR AND THE COMPOSITION AND CONSTITUTION OF THE ALKALI SALTS OF THE NITROPHENOLS.

By J. C. W. Frazer.

The alkali salts of the nitrophenols, so far as they have been made, show quite a wide variation in color, and this difference of color has been studied by Carnelly and Alexander[1] in the case of the sodium and potassium salts of ortho- and paranitrophenol. Since this work of Carnelly and Alexander the subject has not been further investigated and in some cases, notably in the case of metanitrophenol, the number of salts is extremely small. In none of them has either the rubidium or caesium salt been made.

At the suggestion of Professor Remsen I have prepared the sodium, potassium, rubidium, and caesium salts of the three nitrophenols, the object being to see if any connection between their color and composition could be discovered. The salts of these metals were chosen as furnishing the best series for such a study. Of metanitrophenol only the potassium salt is recorded. As the work progressed, 1 : 2 : 3 nitrocresol was included in the list of substances whose salts were made and analyzed.

Ortho- and paranitrophenol were made in the usual way by treatment of phenol with nitric acid, and after separating the oily layer from the acid the orthonitrophenol is distilled off with a current of steam. As the orthonitrophenol comes over in this operation it is sufficiently pure for use. The paranitrophenol is extracted from the tarry mass by hot, strong hydrochloric acid, and this solution boiled with animal charcoal. It is obtained perfectly pure by several recrystallizations in this manner.

Metanitrophenol was obtained from metanitraniline by first diazotizing and boiling the resulting diazo compound with dilute sulphuric acid, and then extracting this solution with ether. During this operation the directions of Bantlin[2] were followed. By recrystallizing from strong hydrochloric acid, as in the case of paranitrophenol, the substance is obtained pure.

In making the 1 : 2 : 3-nitrocresol, orthotoluidine is the starting-point. From this, orthocresol was made. By treatment of the orthocresol with nitric acid in acetic acid solution, action takes place at once,[3] and after standing a short while the whole is poured into water. A brownish-red substance separates out, and from this, by distillation with steam, the 1 : 2 : 3-nitrocresol passes over while the 1 : 2 : 5-nitrocresol, which is formed at the same time, is left behind. In this condition the substance is not quite pure enough for use, but it can be obtained pure by recrystallizing from dilute alcohol. It then melted sharply at 69°.5.

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[1] J. Chem. Soc., 4, 64.

[2] Ber. d. chem. Ges., 11, 2099.

[3] *Ibid.*, 14, 567.

The preparation of the nitrophenolates is a simple matter as they can be obtained from either the carbonates or the hydroxides. In making the nitrocresolates it is best to use the hydroxide of the metal, as the substance is such a weak acid that it is necessary to heat for some time to drive out carbon dioxide completely from carbonates, and this is objectionable on account of the volatility of the nitrocresol with water vapor.

Some of these salts are obtained in pure state only with difficulty. This was found to be true of sodium and caesium orthonitrophenolate and of some of the nitrocresolates. This is probably due to the fact that the salt in solution undergoes slight decomposition while evaporating, and some of the nitrophenol or nitrocresol separates with the salt. That slight decompositions do take place in solutions of these salts is indicated by the fact that the odor of orthonitrophenol and nitrocresol can be observed when the solutions have stood for any length of time. The dry salts too undergo very slow decomposition, the orthonitrophenol and nitrocresol escaping and the substance turning white. This may be due to the tendency of the carbon dioxide of the atmosphere to convert the substances into carbonates.

In order to purify those salts which separated in slightly impure condition, the following method was adopted: The salt was treated in the cold with strong alcohol to free it from any excess of the nitrophenol or nitrocresol. It was then dissolved in hot alcohol, which would leave behind any excess of carbonate. The salt thus extracted was recrystallized from water. The analysis was made as soon as possible, because of the fact that some of the salts undergo slight decomposition on long standing, even when in tightly-corked bottles, as indicated by the odor.

The water of crystallization was not determined, as in some cases decomposition was found to take place. The metal was determined as sulphate and the formula deduced from these results.

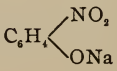
Orthonitrophenolates.

Sodium Orthonitrophenolate.—With this salt concordant results could not be obtained till the method of purification outlined above was applied. Analyses made with each sample were concordant but varied with the sample used. This is shown by the following analyses :

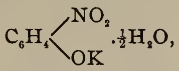
Amount of substance taken. Gram.	Na_2SO_4 found. Gram.	Na found. Per cent.
0.5284	0.2178	13.35
0.7593	0.3116	13.26
0.5189	0.2250	14.04
0.5224	0.2246	13.94
0.5768	0.2348	13.22
0.3283	0.1388	12.90
0.4749	0.1976	13.47
1.0314	0.4429	13.90
1.4349	0.6115	13.80
0.8945	0.3194	14.0
0.9554	0.3389	13.94

Six different samples were made, and in the analyses above recorded the first and second were of one of these samples, the third and fourth of another, the fifth and sixth of another, the seventh of another, the eighth and ninth of another, the tenth and eleventh of another, and in all of them the percentage of sodium is too small for the anhydrous salt. By purifying the salt by the method above the following results were obtained :

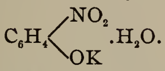
Amount of substance. Gram.	Na_2SO_4 found. Gram.	Na found. Per cent.	Calculated. Per cent.
0.3805	0.1679	14.29	14.28
0.3511	0.1537	14.18	....

This agrees with the formula  $C_6H_4\begin{cases}NO_2\\ONa\end{cases}$. The salt crystallizes, as is well known, in large, splendid, scarlet-red needles, often as much as 2 cm. in length.

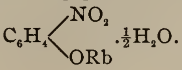
Potassium Orthonitrophenolate.—It is not as difficult to obtain this salt pure as it is to obtain the sodium salt above. It crystallizes from water solution in large, orange-red plates, often as much as a centimeter in length, or in orange-red needles which have been obtained as much as 3 cm. long. This salt has been made and analyzed by Fritzsche,[1] who, from his analysis, assigned to it the formula



$$C_6H_4\left\langle\begin{matrix}NO_2\\OK\end{matrix}\right.\cdot\tfrac{1}{2}H_2O,$$

and later was made by Post and Mehrtens,[2] who gave it the formula  $C_6H_4\left\langle\begin{matrix}NO_2\\OK\end{matrix}\right.\cdot H_2O$. The analyses of this salt made by myself agree with the formula first given it by Fritzsche, as will be seen :

Amount of salt taken. Grams.	K_2SO_4 found. Gram.	K found. Per cent.	Calculated. Per cent.
1.1583	0.5387	20.86	20.96
1.1251	0.5230	20.83	....

Rubidium Orthonitrophenolate.—This salt has not been described. It crystallizes from water in large, beautiful plates resembling very much the corresponding potassium salt above, except that it is slightly lighter in color than this salt. It crystallizes well in orange-yellow crystals, which have a composition analogous to the corresponding potassium salt. It is to be represented by the formula  $C_6H_4\left\langle\begin{matrix}NO_2\\ORb\end{matrix}\right.\cdot\tfrac{1}{2}H_2O$.

Amount of substance taken. Gram.	Rb_2SO_4 found. Gram.	Rb found. Per cent.	Calculated. Per cent.
0.4010	0.2297	36.67	36.74
0.4563	0.2611	36.62	....

As will be seen later, this is the usual form in which the salt crystallizes, but not the only one. There is another variety of this salt and the passage of this last into the more common variety is an interesting one. Of this I shall speak more fully later on.

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[1] Ann. Chem. (Liebig), **110**, 153.

[2] Ber. d. chem. Ges., **8**, 1552.

Caesium Orthonitrophenolate.—This salt has not been previously described. It is very soluble in water but crystallizes from this strong solution in large crystals, having in this respect the tendency, shown by the orthonitrophenolates above, of crystallizing well. It can be obtained pure only with difficulty. The two following analyses, made with different samples, show this :

Amount of salt taken. Gram.	Cs_2SO_4 found. Gram.	Cs found. Per cent.
0.4341	0.2782	47.06
0.2992	0.1931	47.43

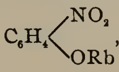
On purification by the method adopted above, the following results were obtained :

Amount of salt taken. Gram.	Cs_2SO_4 found. Gram.	Cs found. Per cent.	Calculated. Per cent.
0.2990	0.1994	48.99	49.07
0.2829	0.1890	49.09	....

This salt differs in crystalline form from the other orthonitrophenolates above described. It crystallizes neither in needles nor in plates, but in thick, massive crystals of a dark scarlet-red color, resembling sodium orthonitrophenolate. By reflected light the crystal faces show a slightly greenish color.

In this series of four orthonitrophenolates, two crystallize without water of crystallization and two with 0.5 molecule of water each. The first two, sodium and caesium orthonitrophenolates have, so far as I have ever noticed, no tendency to crystallize with water of crystallization. On the other hand, it has been found possible to crystallize potassium and rubidium orthonitrophenolate without water of crystallization. Fritzsche had early remarked on the difference in color between sodium and potassium orthonitrophenolate, and had actually tried to obtain the potassium salt in the dark-red variety corresponding to the sodium salt. He tried to do this by crystallizing the salt from alcohol, but found that even from absolute alcohol the salt crystallized in the lighter form and still contained 0.5 molecule of water of crystallization.

On crystallizing the rubidium salt from water it was observed that at times it would crystallize out in dark-red needles, resembling the sodium salt very much, though it was not quite so dark as the latter. On setting the beaker down, the salt in contact with the mother-liquor began to change to the lighter, ordinary variety of the salt. On dissolving the salt by warming the solution, it came down again in the dark variety. But it was found that the salt in this form had such a tendency to pass over into the lighter variety as to make it impossible to filter it off and obtain it in dry condition. When slightly disturbed by touching it with a stirring rod, the change begins at the point of disturbance and passes over the whole mass of crystals. Further, the change can be brought about by sprinkling a small amount of the lighter crystals on the red crystals when they have separated out from the solution. By considering the colors of the orthonitrophenolates described above we might suppose this darker variety of the rubidium salt to be anhydrous like the sodium and caesium salts, which it resembles in color, the change of color being brought about by the change of the salt to the hydrated condition, which is the usual condition in which it separates from water solution.

In order to obtain the salt in pure condition then, if this were true, it would be necessary to exclude water from the solvent used. For this purpose absolute alcohol was chosen as the best solvent. Crystallization was effected from absolute alcohol, but as the time for evaporation at ordinary temperature is so great that the substance begins to change because of absorbing atmospheric moisture, the evaporation was hastened by keeping the solution warm. Under these conditions the salt crystallizes out in red needles, lighter in color than sodium orthonitrophenolate but much darker than the common variety of rubidium orthonitrophenolate. The salt has the formula  $C_6H_4\begin{cases}NO_2\\ORb\end{cases}$, as seen from the following analysis :

Amount of salt taken. Gram.	Rb_2SO_4 found. Gram.	Rb found. Per cent.	Calculated. Per cent.
0.2331	0.1397	38.39	38.23

That the increased temperature can have nothing to do with the change of color is shown by the fact that the same result can be obtained without the aid of heat, by simply causing the evaporation to take place in a dry atmosphere.

I have obtained sodium, rubidium, and caesium orthonitrophenolates in the dark-red variety. The potassium salt alone, of those investigated here, remains and under ordinary circumstances shows no tendency to crystallize in the darker variety. It was this salt which Fritzsche[1] had tried to crystallize in the darker variety. For this purpose he crystallized it from absolute alcohol and presumably in an open vessel. He found that the substance always crystallized in the lighter variety and always contained 0.5 molecule of water.

In using the same solvent as Fritzsche had used, it was soon found that alcohol simply distilled over quicklime still contained enough water to transform the salt, at least to some extent, into the hydrate, so that alcohol which had been distilled over sodium was used. Some potassium orthonitrophenolate was dehydrated by heating in an air-bath to 120°, dissolved in hot, absolute alcohol, and quickly filtered into an Erlenmeyer flask while still hot. The flask and its contents were kept almost at its boiling-point, and air, dried by passing through two wash-bottles containing sulphuric acid, was drawn through the flask. The crystals which separated at first were red and very much like the darker rubidium salt above. As evaporation went on the crystals, which had separated, began to turn lighter, and before evaporation was complete, only the yellow variety remained. The red variety of this salt was not obtained pure until evaporation of the solution was effected in a current of air dried over phosphorus pentoxide. Under these circumstances, the salt crystallizes from absolute alcohol in small, red needles, similar in appearance to the rubidium salt obtained in a similar manner. The remarkable fact brought out by this experiment is that this salt has the power to take up water from air dried over sulphuric acid. It was found by analysis to be the anhydrous salt as seen below:

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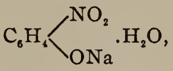
[1] Ann. Chem. (Liebig), 110, 153.

Amount of salt taken. Gram.	Rb_2SO_4 found. Gram.	Rb found. Per cent.	Calculated. Per cent.
0.1915	0.0935	21.88	22.00

Metanitrophenolates.

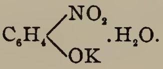
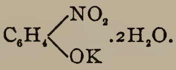
Sodium Metanitrophenolate.—This salt crystallizes in rather small needles of an orange-red color, resembling somewhat potassium orthonitrophenolate. It was found on analysis to have the composition represented by the formula



$$C_6H_4{<}\begin{matrix}NO_2\\ONa\end{matrix}.H_2O,$$

as seen below.

Amount of salt taken. Gram.	Na_2SO_4 found. Gram.	Na found. Per cent.	Calculated. Per cent.
0.2190	0.0771	11.41	11.6

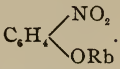
Potassium Metanitrophenolate.—This salt, like sodium metanitrophenolate, crystallizes in small, needle-shaped crystals but are much lighter in color than the latter. They are orange-yellow. On analysis it was found to have the composition represented by the formula  $C_6H_4{<}\begin{matrix}NO_2\\OK\end{matrix}.H_2O$. Post and Mehrtens[1] give it the formula  $C_6H_4{<}\begin{matrix}NO_2\\OK\end{matrix}.2H_2O$.

Amount of substance taken. Gram.	K_2SO_4 found. Gram.	K found. Per cent.	Calculated. Per cent.
0.3206	0.1206	16.89	16.88
0.2793	0.1059	17.03	....

Rubidium Metanitrophenolate.—Two salts of rubidium with metanitrophenol have been isolated, one the neutral salt, the other an acid salt. The difference in color between these two substances is very marked and is suggestive of the difference in color observed in the two forms of rubidium orthonitro-

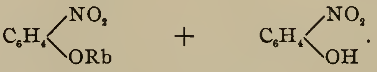
[1] Ber. d. chem. Ges., 8, 1552.

phenolate above. But the difference here is due to another cause.

The lighter of the two is the neutral salt which was shown by analysis to have the formula  $C_6H_4{<}\begin{matrix}NO_2\\ORb\end{matrix}$. It crystallizes in small, yellow, needle-shaped crystals. Its analysis gave the following results:

Amount of substance taken. Gram.	Rb_2SO_4 found. Gram.	Rb found. Per cent.	Calculated. Per cent.
0.3459	0.2065	38.27	38.2

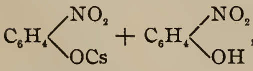
The acid salt mentioned above crystallizes in clusters of well-formed, needle-shaped crystals, radiating from a common point. They are of brownish-red color by transmitted light and brown by reflected light, and have the composition represented by the formula



$$C_6H_4{<}\begin{matrix}NO_2\\ORb\end{matrix} + C_6H_4{<}\begin{matrix}NO_2\\OH\end{matrix}.$$

The analysis gave the following results:

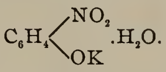
Amount of salt taken. Gram.	Rb_2SO_4 found. Gram.	Rb found. Per cent.	Calculated. Per cent.
0.4031	0.1485	23.58	23.5

Caesium Metanitrophenolate.—This salt crystallizes in beautiful, almost blood-red crystals, which resemble caesium orthonitrophenolate in color, but the color is clearer and a more brilliant red. It is, like one of the rubidium salts above, an acid salt, having the composition represented by the formula  $C_6H_4{<}\begin{matrix}NO_2\\OCs\end{matrix} + C_6H_4{<}\begin{matrix}NO_2\\OH\end{matrix}$, as seen from the following analytical results:

Amount of salt taken. Gram.	Cs_2SO_4 found. Gram.	Cs found. Per cent.	Calculated. Per cent.
0.2854	0.1261	32.46	32.4

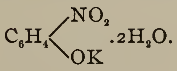
Paranitrophenolates.

Sodium Paranitrophenolate.—This salt crystallizes from water in large, lemon-yellow prisms, which on standing exposed for even a short time lose their transparency and become opaque without any noticeable change of color. This change has been studied and found, as was to be expected, to be due to loss of water of crystallization. As the salt first crystallizes, it contains 4 molecules of water of crystallization, and on standing exposed to the air two of these are given off.

Potassium Paranitrophenolate.—This salt differs from the others by its lack of crystallizing power. On evaporating slowly it was found to come down as a lemon-yellow, crystalline powder. On analysis it was found to have the composition represented by the formula  $C_6H_4\left\langle\begin{array}{l}NO_2\\ OK\end{array}\right. .H_2O$.

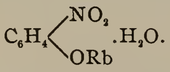
Amount of salt taken.	K_2SO_4 found.	K found.	Calculated.
Gram.	Gram.	Per cent.	Per cent.
0.2592	0.1172	20.26	20.0
0.2323	0.1052	20.29	....

This salt has been made and analyzed by Post and Mehrtens,[1] who found it to have the composition



$$C_6H_4\left\langle\begin{array}{l}NO_2\\ OK\end{array}\right. .2H_2O.$$

Rubidium Paranitrophenolate.—This salt crystallizes from water in large, bright-yellow scales having the composition



$$C_6H_4\left\langle\begin{array}{l}NO_2\\ ORb\end{array}\right. .H_2O.$$

Amount of salt taken.	Rb_2SO_4 found.	Rb found.	Calculated.
Gram.	Gram.	Per cent.	Per cent.
0.2111	0.1161	35.2	35.3
0.2277	0.1250	35.14	....

Rubidium paranitrophenolate crystallizes from water in beautiful, well-formed, yellow needles, which, when filtered off, begin to break up at once into small parts, a change which may probably be due to loss of water of crystallization, as in the case of sodium paranitrophenolate. The rapidity of the change made it impossible to obtain the substance in a state of sufficient purity for analysis.

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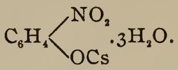
[1] Ber. d. chem. Ges., 8, 1552.

Caesium Paranitrophenolate.—This salt crystallizes in large, lemon-yellow plates having the composition



$$C_6H_4\begin{cases}NO_2\\OCs\end{cases}.3H_2O.$$

Amount of salt taken. Gram.	Cs_2SO_4 found. Gram.	Cs found. Per cent.	Calculated. Per cent.
0.2234	0.1240	40.78	40.9
0.3371	0.1872	40.81	....

1 : 2 : 3-Nitrocresolates.

Nitrocresol is a weaker acid than the nitrophenols, and, being a volatile substance, its salts are more easily decomposed, and it is harder to obtain them pure. This seemed especially true of the caesium salt, solutions of which, when left to evaporate, underwent continuous decomposition with separation of nitrocresol. This may have been caused by the slow and continuous action of carbon dioxide of the atmosphere, the odor of nitrocresol being always noticeable from solutions of its salts. On account of the weak acid properties of nitrocresol its salts are made from the hydroxides of the metals, and the purification of the salts is the same as in the case of the nitrophenolates.

Sodium Nitrocresolate.—This salt crystallizes from water solution in small, light-red needles, having the composition given by the formula $C_6H_3(NO_2)CH_3.ONa.2H_2O$.

Amount of salt taken. Gram.	Na_2SO_4 found. Gram.	Na found. Per cent.	Calculated. Per cent.
0.4165	0.1398	10.85	10.90
0.3672	0.1243	10.90	....

Potassium Nitrocresolate.—This salt crystallizes in light-red scales, resembling the sodium salt above. Its color is slightly lighter, and it has the composition represented by the formula $C_6H_3(CH_3)(NO_2)OK.\frac{1}{2}H_2O$.

Amount of salt taken. Gram.	Rb_2SO_4 found. Gram.	Rb found. Per cent.	Calculated. Per cent.
0.1752	0.0760	19.45	19.5
0.3233	0.1413	19.66	....

Rubidium Nitrocresolate.—This salt crystallizes in beautiful, cherry-red scales having a very high luster. By slow evaporation the salt is deposited in well-formed, monoclinic, diamond-shaped crystals of dark, cherry-red color. It has the composition $C_6H_3(CH_3)(NO_2)ORb.H_2O$.

Amount of salt taken. Gram.	Rb_2SO_4 found. Gram.	Rb found. Per cent.	Calculated. Per cent.
0.2127	0.1122	33.59	33.4

Caesium nitrocresolate was made but, as has been stated above, at each recrystallization partial separation of the nitrocresol took place so that the salt was not obtained pure enough for analysis. For some reason this salt was more unstable than the others. It is, however, of a red color, resembling sodium nitrocresolate in this respect.

The conductivity of ortho- and paranitrophenol has been determined by Hantzsch,[1] who gives the following tables :

Paranitrophenol (*at* 25°).		*Orthonitrophenol* (*at* 25°).	
v.	μ_v. Per cent.	v.	μ_v. Per cent.
64	0.89	128	1.13
128	1.28	256	1.52
256	1.79	512	2.17
512	2.53	1024	3.14

These results differ considerably from those of Bader,[2] who found numbers considerably greater than these.

The determinations of my own, below, differ somewhat from those of Hantzsch and Schümann, but all of the three sets of determinations agree fairly well for a substance of such low conductivity, and they all show that orthonitrophenol is a slightly weaker acid than paranitrophenol, while metanitrophenol is a somewhat stronger acid than paranitrophenol.

Paranitrophenol (*at* 25°).		*Metanitrophenol* (*at* 25°).		*Orthonitrophenol* (*at* 25°).	
v.	μ_v. Per cent.	v.	μ_v. Per cent.	v.	μ_v. Per cent.
32	0.924	32	1.18	128	1.02
64	1.201	64	1.20	256	1.85
128	1.567	128	1.52	512	2.38
256	1.752	256	2.01	1024	3.77

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[1] Ber. d. chem. Ges., 32, 3066.

[2] Ztschr. phys. Chem., 6, 289.

From my own determinations, meta- and paranitrophenol are dissociated to about the same extent, while both are dissociated somewhat more than orthonitrophenol.

The absorption spectra of some of the salts of ortho- and paranitrophenol were examined but nothing of any apparent value was found. When in concentrated solution these substances were found to absorb all the violet end of the spectrum, even down through the yellow in the case of orthonitrophenolates. On diluting, more and more of the violet end of the spectrum was transmitted until, at great dilutions, only a diminution of the intensity of the violet end was noticed, without, at any time, a tendency to show a banded spectrum. The only difference in the case of solutions of paranitrophenolates is that the light is not absorbed so far down towards the red end of the spectrum as is the case with the same dilution of an orthonitrophenolate.

Carnelly and Alexander[1] have found :

(1) That without exception the color passes toward the red end of the spectrum as the temperature rises.

(2) That the color of the ortho compound is nearer the red end than the corresponding para compound. Para compounds have a higher melting-point than ortho compounds. The latter he concludes from this to be at a relatively higher temperature and according to this should have a color nearer the red end of the chromatic scale than the higher melting, para compound, which accords with the first conclusion above.

(3) By a comparison of the nitrophenolates of the same sub-group the color passes toward the red end as the atomic weight increases.

(4) The color passes toward the red end of the chromatic scale as the amount of water decreases.

Summary.

(1) Speaking in a general way concerning the color of the salts described above of the three classes of nitrophenolates, it may be said that the orthonitrophenolates possess a color that is nearest the red end of the chromatic scale, while the

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[1] *Loc. cit.*

metanitrophenolates come next, and the paranitrophenolates are furthest removed from the red end.

(2) There is a gradation of color in the case of each series of nitrophenolates above, and in the direction pointed out in the third conclusion of Carnelly and Alexander above, that is, the color growing lighter in each series as the atomic weight of the metal increases. This, however, is not very noticeable in the paranitrophenolates as only little difference of color is observed in passing from one salt to the other in the series.

(3) In the same way, water of crystallization causes little change of color in the paranitrophenolates, while the change of color due to water of crystallization is greatest in the case of the orthonitrophenolates, and next in order in this respect come the metanitrophenolates.

(4) Paranitrophenol and metanitrophenol have the power of forming acid salts, while orthonitrophenol has not been found to have this power.

(5) The orthonitrophenolates above described are all red when dehydrated. This is also true of the metanitrophenolates though these are lighter than the orthonitrophenolates.

(6) Paranitrophenolates, with the exception of the sodium salt, are yellow when anhydrous and cold. The sodium salt is reddish.

(7) The nitrocresolates are all red, though not as dark as the orthonitrophenolates. In the case of the nitrocresolates, the variation in color from one salt to another is less than in the case of ortho- and metanitrophenolates. Water does not cause as great a change in the color of the nitrocresolates and of the paranitrophenolates as in the case of the other nitrophenolates.

JOHNS HOPKINS UNIV.,
June, 1901.

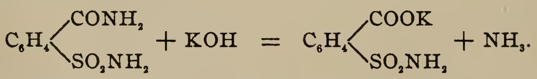
COMPARATIVE STUDY OF THE METASULPHAMINEBENZOIC ACIDS MADE BY DIFFERENT METHODS.

BY J. C. W. FRAZER.

Metasulphaminebenzoic acid has been made by several workers and by several methods, and the lack of agreement which is found in their descriptions of the properties of the substance calls for a more careful study of the substance made in different ways. The point of greatest difference is in the melting-point which different investigators have found for the substance. Even when using the same method, different workers have found melting-points that differ quite markedly from one another. In fact, from these results it might fairly be doubted whether the same substance had always been under investigation, though the methods employed would leave little room for such doubt. For this reason, Professor Remsen suggested to me to prepare this substance by several methods and to determine whether the same product is always obtained and, so, to settle the question concerning its melting-point.

In view of the interesting influence which continued heating has been found to produce on parasulphaminebenzoic acid and of similar work that has been done in this laboratory on metasulphaminebenzoic acid itself, a definite statement concerning the melting-point of metasulphaminebenzoic acid acquires more than ordinary significance.

Metasulphaminebenzoic acid was first obtained by Limpricht and Uslar[1] from metasulphobenzoic diamide by heating with potassium hydroxide. Under these conditions the carbamine group is saponified and the sulphamine acid is precipitated on acidifying :



$$C_6H_4\left\langle\begin{matrix}CONH_2\\SO_2NH_2\end{matrix}\right. + KOH = C_6H_4\left\langle\begin{matrix}COOK\\SO_2NH_2\end{matrix}\right. + NH_3.$$

The authors describe the substance as separating in crystals resembling potassium chlorate. They did not determine its melting-point but found the substance to melt somewhere above 200°.

Remsen and Palmer[2] obtained the acid from metatoluenesulphone amide by oxidation with potassium permanganate. They found the substance they obtained to melt at 235° (uncorrected), at the same time suffering slight decomposition.

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[1] Ann. Chem. (Liebig), **106**, 36, 37, 42–46.

[2] This JOURNAL, **4**, 144.

Noyes and Walker[1] have made the acid from metatoluenesulphone amide by oxidation with potassium ferricyanide. The potassium salt of the acid they obtained was washed with strong alcohol to remove any unoxidized amide. The acid liberated from this salt they found to have a melting-point of 246° to 247° (uncorrected).

W. Jones[2] has made the acid by three different methods: First, by a slight modification of the method of Limpricht and Uslar, when he obtained an acid melting at 248° (uncorrected). Next he obtained the acid by saponification of metasulphaminebenzoic nitrile with dilute caustic potash. The nitrile itself he obtained from the diamide by treatment with phosphorus pentachloride and, after distilling off the phosphorus oxychloride, crystallizing the product from warm water. The acid obtained in this way was the same as that from the first method above. Of the second method he says: "No method is better adapted to the preparation of the acid in pure condition than this one."

He obtained metasulphaminebenzoic acid by treatment of metasulphobenzoic chloride with aqueous ammonia. The acid obtained by this method he found to melt at 248° to 248°.5.

Griffin[3] obtained metasulphaminebenzoic acid by oxidation of metatoluenesulphone amide with chromic acid. On purifying, he obtained a substance melting at 233° (uncorrected).

Nakaseko,[4] working in this laboratory, next made the substance. He obtained the acid by the method recommended by Jones as being the best, the saponification of metasulphaminebenzonitrile. After recrystallizing the acid several times, he found it to melt at 237° to 238° (corrected). He then converted the acid into the ammonium salt and recrystallized this. The purified ammonium salt was converted into the lead salt and this in turn recrystallized several times. The acid was liberated from the lead salt by treatment with sulphuric acid and then recrystallized several times. During this treatment he found the melting-point had remained unchanged at 237° to 238°.

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[1] This Journal, 8, 188.

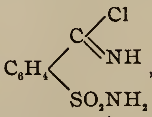
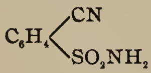
[2] Private communication.

[3] This Journal, 19, 180.

[4] Dissertation, 1898.

It was because of this variation that the following work was undertaken.

Metasulphobenzoic diamide was made from acid potassium metasulphobenzoate by treatment with phosphorus pentachloride. Metasulphobenzoic dichloride thus obtained is treated with aqueous ammonia when the diamide is obtained. This diamide is saponified with caustic potash by the method used by Jones, and the product acidified with hydrochloric acid. When the metasulphaminebenzoic acid crystallizes out the precaution mentioned by Jones is observed, that is, the solution is not allowed to become perfectly cold, otherwise the unchanged diamide separates along with the sulphamine acid. The substance thus obtained was recrystallized four times, observing the same precaution. This substance had a melting-point of 238°. When recrystallized a fifth time in the same way, after boiling with animal charcoal, the melting-point 237°.5 was obtained. Some of this product was then converted into the barium salt by treatment with barium carbonate and the barium salt recrystallized from water and repeatedly washed with 95 per cent alcohol, recrystallized, warmed with 95 per cent alcohol, and, after cooling, washed with alcohol and again recrystallized from water. From the salt thus purified the acid was liberated by treatment with hydrochloric acid, and the acid recrystallized from hot water. The metasulphaminebenzoic acid crystallized in beautiful, colorless scales, which melted at 237°.5 to 238° (corrected).

The metasulphobenzoic diamide above is then treated with phosphorus pentachloride, which converts it into metasulphaminebenzonitrile hydrochloride,  $C_6H_4<\begin{matrix}C<\begin{matrix}Cl\\NH\end{matrix}\\SO_2NH_2\end{matrix}$, which, when dissolved in warm water, forms metasulphaminebenzoic nitrile,  $C_6H_4<\begin{matrix}CN\\SO_2NH_2\end{matrix}$. This substance is boiled five hours with dilute caustic potash. At the end of this time, on acidifying with hydrochloric acid, a voluminous precipitate separates which does not crystallize anything like the metasulphaminebenzoic acid. It can be separated by fractional crystallization into a crystalline portion, from which the sulphamine acid can be obtained in pure condition. Not a very good yield of the sulphamine acid was obtained, and the large amount of precipitate formed may have been the acid potassium salt which came down on acidifying, though this was not determined. After six recrystallizations the acid had every appearance of the metasulphaminebenzoic acid made by the method above, and was found to have the melting-point 237° to 238° (corrected).

Crude paratoluidinemetasulphonic acid was purified by boiling the solution acidified with hydrochloric acid and adding animal charcoal. Nitrogen trioxide was conducted into a thin paste made by mixing this with alcohol, according to the method given by Griffin.[1] The diazo compound thus obtained was decomposed in absolute methyl alcohol in presence of anhydrous sodium carbonate, according to the directions of the same author. After the decomposition of the diazo compound is complete, the alcohol is evaporated off, and the dried residue converted into metatoluenesulphone chloride by treatment with phosphorus pentachloride, and this, on treatment with aqueous ammonia, is converted into metatoluenesulphone amide. This amide was oxidized with chromic acid according to the directions given by Griffin. To free the acid formed from the unoxidized toluenesulphone amide, it is converted into the potassium salt. On liberating the free metasulphaminebenzoic acid and recrystallizing several times it was found to have all the appearance of that obtained by the methods above, and was found to have the melting-point 237°.5 to 238°.5 (corrected).

The metasulphaminebenzoic acid was next made from parabrommetatoluenesulphonic acid. The reduction of this acid has been accomplished by Müller[2] by treating its aqueous solution with sodium amalgam. For the complete removal of the bromine the action is continued for about eight days. At the end of that time it is found that no bromine is left in the acid. The solution is then acidified with sulphuric acid and evaporated when, by allowing it to cool, a great deal of the potassium sulphate can be eliminated. The solution thus obtained from the sulphate, which has separated, is then evaporated to dryness and treated with phosphorus pentachloride. The oily chloride, after it has been washed with water, is converted into the amide by treatment with aqueous ammonia. The metatoluenesulphone amide thus obtained is oxidized with chromic acid as above, and the metasulphaminebenzoic acid obtained is purified in the same way. The substance had every appearance of that already obtained and melted at 237°.5 to 238° (corrected).

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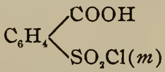
[1] This Journal, 19, 164.

[2] Ann. Chem. (Liebig), 169, 347.

The acid was next obtained from the metasulphone chloride of benzoic acid,  $C_6H_4\left\langle\begin{array}{l}COOH\\SO_2Cl(m)\end{array}\right.$, by treatment with aqueous ammonia. This chloride was obtained from benzoyl chloride by treating it with sulphur trioxide. The sulphonic acid group enters the position meta to the carbonyl group, and by an action not yet understood the above substance is obtained. This, as stated, gives the metasulphaminebenzoic acid on treatment with aqueous ammonia and was found to melt at 237°.5.

The thermometer used in all this work was carefully compared with two standard thermometers and the corrections always applied.

There was one other point concerning the melting-point of this acid which was tested.

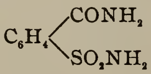
It is stated by Jones that his metasulphaminebenzoic acid could not be made to melt below 248°. He kept a small quantity of the acid at a temperature of 240° to 242° for an hour. The temperature was then gradually raised and while doing so was kept at temperatures from 242° to 246° for three hours, but the acid would not melt below 248°. On the other hand, Nakaseko found quite different results when proceeding in a similar way. While he found the melting-point of the metasulphaminebenzoic acid to be 237° to 238° he says it can be melted considerably lower than this.

After drying the acid carefully in an air-bath at 140° for two hours, it was placed in specimen tubes and heated for four hours at 210° to 215°. At the end of this time it did not melt, but by raising the temperature slowly till it reached 220° it melted completely.

I placed about 1 gram of the dried metasulphaminebenzoic acid in a specimen-tube and heated it for one hour at 215° (once the temperature rose to 220° for a short time), and at the end of this time the substance had melted. This result is similar to that of Nakaseko, above referred to.

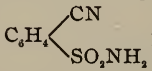
This being the case, in determining the melting-point of metasulphaminebenzoic acid made by the different methods above, the substance was heated as rapidly as possible till near the melting-point so as to avoid any change of the melting-point such as was found above to be caused by continued heating.

It will thus be seen that metasulphaminebenzoic acid, whether made (1) from metasulphobenzoic diamide,

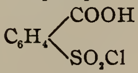


$C_6H_4\begin{cases}CONH_2\\SO_2NH_2\end{cases}$;

(2) from metasulphaminebenzoic nitrile,

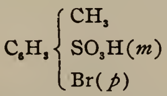


$C_6H_4\begin{cases}CN\\SO_2NH_2\end{cases}$; (3) from the metasulphone chloride of benzoic acid,



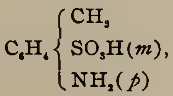
$C_6H_4\begin{cases}COOH\\SO_2Cl\end{cases}$;

(4) from parabrommetatoluenesulphonic acid,



$$C_6H_3\begin{cases}CH_3\\SO_3H(m)\\Br(p)\end{cases};$$

or (5) from paraminometatoluenesulphonic acid,



$$C_6H_4\begin{cases}CH_3\\SO_3H(m),\\NH_2(p)\end{cases}$$

is one and the same product. When heated rapidly it melts at 237° to 238° (corrected). When heated slowly it undergoes a change that causes it to melt as low as 215°.

JOHNS HOPKINS UNIV.,
June, 1901.

Contributions from the Sheffield Laboratory of Yale University.

CXI.—ON THE THIOCYANATES OF SILVER AND POTASSIUM AND THEIR SOLUBILITY.

BY H. W. FOOTE.

INTRODUCTION.

The main object of the present investigation has been to devise a method for determining what double salts are formed by two single salts with a common ion. The method depends chiefly on well-known principles of solubility.

The conditions regulating the solubility of two salts with a common ion are well known.[1] At a given temperature there will be but one saturated solution possible when both salts are present in excess, provided the salts form no double salts with each other. If one double salt *AB* forms from the two single salts *A* and *B*, there will be two definite saturated solutions, one when *A* and *AB* are both present as solids and the other when *AB* and *B* are present. The single salts alone or a double salt alone can exist in contact with a series of saturated solutions containing *A* and *B*. It follows that when two separate salts are present in the residue, the composition of this residue will change as the relative proportion of the two salts changes, but the composition of the saturated solution remains constant. When, however, only one salt, either simple or double, is in the residue, its composition must remain fixed while the composition of the saturated solution varies within certain limits. We have then the rule that if the composition of the residue varies in different determinations while the solution remains constant, a mixture of two salts is present. If the solution varies while the residue remains constant in composition, a single salt or one double salt is present. The method of determining double salts by solubility determinations is based on this rule. A somewhat similar method has been used in investigating the periodides of caesium.[1]

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[1] Ostwald: Lehrb. d. allgem. Chem., 1, 1076; Van 't Hoff: Vorles. über Bild. u. Spalt. von Doppelsalzen.

The investigation has been carried out with the thiocyanates of silver and potassium. Their double thiocyanates have been prepared recently by Wells and Merriam,[2] who described the following compounds:

3KSCN.AgSCN, 2KSCN.AgSCN, and KSCN.AgSCN.

In testing the method on these salts, it has been shown that the salt 3KSCN.AgSCN is unstable under ordinary conditions of temperature. It readily passes over into a mixture of 2KSCN.AgSCN and potassium thiocyanate.

EXPERIMENTAL.

In carrying out the experimental work, accurately weighed quantities of potassium and silver thiocyanates were placed together in a strong glass tube, about the size of a test-tube, and treated with a known amount of water. The quantities of salt and water were so regulated that there was always an undissolved residue at the temperature of the experiment. The relative amounts of each salt were varied systematically in the different determinations. The mixtures were heated for some time, when possible, till both salts dissolved completely, and then placed in a Noyes solubility-apparatus at 25° C. After saturation had taken place, a small amount of solution was removed and analyzed. The composition of the residual thiocyanates could then be calculated with sufficient accuracy. This method of determining the composition of the undissolved salt could be used here, as it was known that all salts formed were anhydrous. In a case where salts contain water of crystallization, it would be necessary to analyze the residue instead of calculating its composition. In one or two cases this was done as a check on the calculated value. When the residue is analyzed, it is unnecessary to weigh accurately the quantities of salts and water used in the experiments.

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[1] Foote: This JOURNAL, **29**, 203 (1903).

[2] *Ibid.*, **28**, 265.

It should be mentioned that it was found difficult to saturate the solutions in which uncombined silver thiocyanate was present as solid phase. Constant results in this case were obtained only when the mixtures were kept at 25° for about a week, shaking them in the apparatus during the day.

The solutions were analyzed as follows: Weighed quantities of solution were treated with water, precipitating silver thiocyanate, which was filtered on a Gooch crucible, dried at 100° to 120° C., and weighed. A small quantity of ferric alum was added to the filtrate, which was acidified with nitric acid, and titrated with standard silver nitrate till just decolorized.

The results obtained are in Table I. Column I. gives the number of the experiment; Columns II. and III., the parts by weight of potassium thiocyanate and silver thiocyanate, respectively, in 100 parts by weight of solution; Columns IV. and V., the percentage of potassium thiocyanate and silver thiocyanate in the residue. The results are separated into groups whose significance will become apparent:

Table I.

I.	II. KSCN in solution.	III. AgSCN in solution.	IV. KSCN in residue.	V. AgSCN in residue.
1	70.38	....	100.0	....
2	70.68	....	100.0	....
3	66.44	9.46	87.95	12.05
4	66.80	8.95	74.29	25.71
5	66.42	9.56	55.25	44.75
6	64.47	10.62	53.38	46.62
7	61.25	11.76	53.97	46.03
8	58.34	13.55	54.23	45.77
9	53.21	17.53	54.14	45.86
10	50.55	20.46	49.12	50.88
11	50.81	20.40	43.98	56.02
12	49.43	20.32	36.58	63.42
13	32.51	18.34	36.75	63.25
14	24.68	16.41	36.26	63.74
15	23.89	16.14	32.83	67.17
16	23.83	16.01	24.66	75.34

Discussion of the Results.

In the above table, experiments Nos. 1 and 2 represent the solubility of pure potassium thiocyanate. Nos. 3, 4, and 5 show a constant solubility while the composition of the residue changes. This indicates that a mixture of potassium thiocyanate and the first double salt is present. Nos. 6, 7, 8, and 9 have a constant composition in the residue while the solution varies. Here the first double salt appears in pure condition. It is evidently 2KSCN.AgSCN. The pure salt contains 53.92 per cent of potassium thiocyanate. Nos. 10 and 11 have a constant solubility and variable composition of the residue corresponding to a mixture of 2KSCN.AgSCN and the next double salt. Nos. 12, 13, and 14 show variable composition of the solution while the residue corresponds closely to KSCN.AgSCN. The pure salt contains 36.90 per cent of potassium thiocyanate. Nos. 15 and 16 have a constant composition of the solution while the residue varies, corresponding to a mixture of KSCN.AgSCN and silver thiocyanate. The experiments were not carried beyond this point as unchanged silver thiocyanate could be seen in the residue.

The results in Table I. are shown graphically in Fig. I.

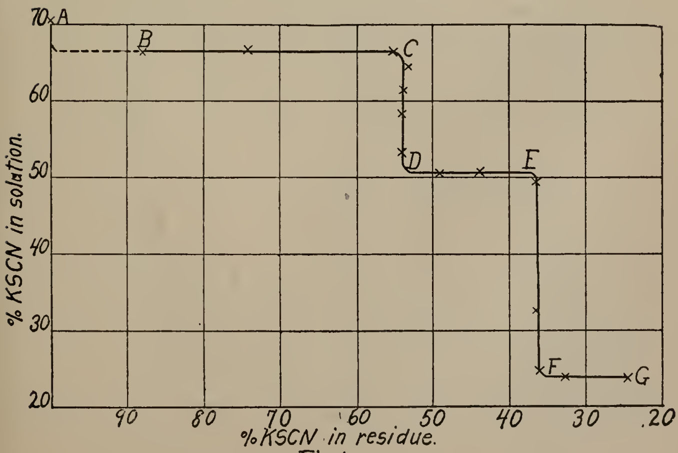

Fig. I.

The percentage of potassium thiocyanate in the solution is plotted as ordinate and the percentage of the same salt in the residue as abscissa. The point *A* represents the solubility of the pure salt. From *B* to *C* the solubility remains constant while the composition of the residue changes, corresponding to the mixture of potassium thiocyanate and 2KSCN.AgSCN. From *C* to *D* the solubility changes, while the residue consists of pure 2KSCN.AgSCN. *DE* shows a mixture of the two salts 2KSCN.AgSCN and KSCN.AgSCN in the residue. Along the curve *EF* only KSCN.AgSCN is present, while along *FG* this salt and silver thiocyanate are present.

The solubility results alone may be shown graphically without regard to the composition of the residue, by plotting the quantities of silver and potassium thiocyanates found in a definite quantity of water. For this purpose the solubility results in Table I. have been recalculated to obtain the molecules of potassium and silver thiocyanates in 100 molecules of water. Where two solids are present, giving a constant solubility, the average results have been used. These recalculated results are given in Table II. The numbers in the first column refer to the corresponding results in Table I.

Table II.—Solubilities Recalculated from Table I.

	Molecules KSCN in 100 molecules H_2O.	Molecules AgSCN in 100 molecules H_2O.
1, 2	44.36	0
3, 4, 5	51.13	4.19
6	47.98	4.60
7	42.07	4.72
8	38.47	5.23
9	33.71	6.50
10, 11	32.52	7.67
12	30.29	7.28
13	12.26	4.05
14	7.77	3.02
15, 16	7.36	2.90

These results are plotted in Fig. II. The molecules of potassium and silver thiocyanates in 100 molecules of water are plotted respectively as ordinate and abscissa.

The point *A* represents the solubility of pure KSCN.

The point *B* represents the solubility of KSCN and 2KSCN.AgSCN.

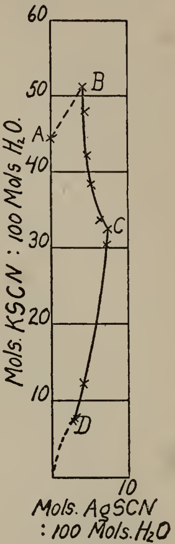

Fig. 2.

The point *C* represents the solubility of 2KSCN.AgSCN and KSCN.AgSCN.

The point *D* represents the solubility of KSCN.AgSCN and AgSCN.

The dotted lines indicate the solubility of potassium or silver thiocyanate when alone in the residue with varying amounts of both salts in solution.

The form of these curves was not directly determined.

The sharp changes in the direction of the curve in Fig. II. indicate the changes of the solid phase with sufficient clearness, but this method gives no clue as to what solid phase is present along any one curve.

The objection might be raised to the solubility results which have been given, that the solubilities obtained were not what they would be in case the double salts themselves were used as a starting-point instead of the single salts. For the sake of comparison, solubility determinations were made in a few cases, using double salts which had previously been prepared, instead of the separate salts. The results are given in Table III., together with the average of the corresponding results taken from Table I.

Table III.

Solubility of KSCN with 2KSCN.AgSCN.

	Double salt and KSCN used.	Single salts used.
KSCN	66.46	66.65
AgSCN	9.60	9.32

Solubility of 2KSCN.AgSCN with KSCN.AgSCN.

	Double salts used.	Single salts used.
KSCN	50.91	50.68
AgSCN	20.41	20.43

Solubility of KSCN.AgSCN with AgSCN.

	Double salt and AgSCN used.	Single salts used.
KSCN	23.88	23.86
AgSCN	16.05	16.08

The results agree as well as would be expected.

The Unstable Salt $3KSCN.AgSCN$.

The formation of the 2 : 1 and 1 : 1 double salts has been demonstrated conclusively by solubility experiments, but there has been no indication of the 3 : 1 salt. If this salt, containing 63.70 per cent of potassium thiocyanate had formed, the solubility in Experiments 3 and 4, Table I., in which the residues correspond in composition to a mixture of potassium thiocyanate and the 3 : 1 salt, would have been different from the solubility in Experiment 5, where the composition of the residue corresponds to a mixture of the 3 : 1 and 2 : 1 salts. There would also have been a break in the curve *BC*, Fig. I.

The 3 : 1 salt can be prepared exactly according to the directions of Wells and Merriam, by dissolving 30 grams of silver thiocyanate and 100 grams of potassium thiocyanate in a small amount of water. Crystals are often obtained several centimeters in length. In the original description of the salt it was mentioned that it turns opaque on standing in the air, and the suggestion was made that it breaks down into another double salt and potassium thiocyanate. It is evident from the solubility experiments that this is what takes place, the salt giving potassium thiocyanate and the 2 : 1 double salt. As this is a very unusual occurrence in double salts, the matter was studied somewhat more closely. Some of the 3 : 1 salt was mixed with potassium thiocyanate and mother-liquor from the double salt and the solubility determined at 25°. The results obtained were :

	Percentage of salt in solution.
KSCN	67.01
AgSCN	9.01

These results agree closely with the results obtained in Experiments 3, 4, and 5, Table I., where a mixture of the 2 : 1 and potassium thiocyanate was present. The 3 : 1 salt gradually turns opaque in the air. Heated in the oven to about 90°, it turns opaque in a few minutes. The transformation was also observed to take place spontaneously when the salt was under the mother-liquor. The white, transformed area gradually spreads through a large crystal looking like a white fungus growth. By bringing a crystal of the 2 : 1 salt in contact with the 3 : 1 under the mother-liquor the transformation could readily be started. This could not be accomplished by using potassium thiocyanate instead of the 2 : 1 salt. In fact, a crop of the 3 : 1 salt mixed with potassium thiocyanate has been obtained. The crystals of each kind were separated from each other mechanically and analyzed to identify them. The 3 : 1 salt in this case was in large, well-formed crystals, and from its appearance had evidently not changed. When the 3 : 1 salt is shaken with potassium thiocyanate, however, it breaks down, as the solubility results indicate, which were given above.

A solution which had deposited the 3 : 1 salt was further impregnated with a small crystal of the 3 : 1 salt, which had turned opaque. More crystals formed, which were separated from the first crop of 3 : 1, and analyzed. They were found to be the pure 2 : 1 salt, as is shown by the following result :

	Calculated for 2KSCN.AgSCN.	Found.
KSCN	53.92	54.28

The above observations are sufficient to prove conclusively that the 3 : 1 salt is unstable at ordinary temperatures, and passes into a mixture of potassium thiocyanate and 2KSCN. AgSCN. So far as I am aware, no similar case has been observed. It appears to be another illustration of the fact observed by Ostwald[1] that an unstable condition of a system often results in preference to a stable condition.

A transition temperature, above or below which the 3 : 1 salt becomes the stable form, could not be discovered. A large crystal which had begun to change was left out of doors over night under the mother-liquor at a temperature slightly above 0°-C. and the transformation progressed steadily. A dilatometer filled with the 2 : 1 salt and potassium thiocyanate and moistened with the mother-liquor saturated with the salts showed no irregular contraction or expansion when cooled to —10° C. If the transition temperature lies below the temperatures investigated, it follows that the reaction

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[1] Ztschr. phys. Chem., 22, 306 (1897).

$$3KSCN.AgSCN = 2KSCN.AgSCN + KSCN$$

takes place with absorption of heat. If the transition temperature is high the reaction takes place with evolution of heat. If this heat effect is appreciable, it could be determined by determining the heat of solution of the 3 : 1 salt before and after it had been transformed.

An attempt was made to do this. The 3 : 1 salt was freed from the mother-liquor between filter-paper and thoroughly air-dried. A part of the crop was then warmed a few minutes at 80° to 90° C. till it turned opaque. The heat of solution of the two products was then determined in a calorimeter, using the same amount of salt in each case and keeping all conditions as nearly alike as possible. The experiment was repeated on a different crop of the salt under somewhat different conditions from those before, but again maintaining the conditions throughout as nearly constant as possible. The following results were obtained :

	Heat of solution of 3KSCN.AgSCN. *a.*	Heat of solution of 2KSCN.AgSCN + KSCN. *b.*	Difference in heat of solution. *b—a.*
1	—23.1 Cal.	—22.5 Cal.	+0.6 Cal.
2	—21.1 "	—20.3 "	+0.8 "

The results in the two sets of experiments do not agree very closely, which is perhaps explained by the fact that it is very difficult to obtain the 3 : 1 salt in perfectly pure condition, forming as it does from a mother-liquor containing 70 or 80 per cent of dissolved salts. The difference between the heat of solution of the 3 : 1 salt and the opaque material is very slight, but indicates that the transition temperature lies below the temperatures investigated. This point can hardly be regarded as definitely settled, however.

Summary.

The results in the preceding article may be summarized as follows :

1. A method depending in part on well-known principles of solubility has been devised for determining all the stable double salts formed by two single salts with a common ion at a given temperature.

2. The method has been applied to determine the double thiocyanates of silver and potassium.

3. The double salt, $3KSCN.AgSCN$, has been shown to be unstable under ordinary conditions of temperature, breaking down readily into $2KSCN.AgSCN$ and potassium thiocyanate.

4. It is probable that this unstable salt becomes stable only at a low temperature, if at all.

New Haven, Conn., February, 1903.

Contributions from the Sheffield Laboratory of Yale University.

CXII.—ON THE DOUBLE CAESIUM AND MERCURIC CHLORIDES AND THEIR SOLUBILITY.

By H. W. Foote.

In the previous article the determination of the double thiocyanates of silver and potassium by means of the solubility of a series of mixtures of the two salts was described. Caesium and mercuric chlorides form one of the largest series of double salts known, and it seemed of interest to apply the method to this series.

The double salts have been described by Wells.[1] They have the following formulas: $3CsCl.HgCl_2$, $2CsCl.HgCl_2$, $CsCl.HgCl_2$, $CsCl.2HgCl_2$, $CsCl.5HgCl_2$. The solubility results have confirmed the existence of these salts, and have shown that others do not exist at the temperature investigated.

The solubility determinations were carried out much as in the previous investigation. An accurately weighed quantity of mercuric chloride was usually treated with a known quantity of water and warmed somewhat, when caesium chloride was added and the mixture warmed in the solubility-tube. The mixtures were then placed in the thermostat at 25°, usually for forty-eight hours. They were rotated about half that time. In only a few cases, where caesium was present in excess, did the mixtures dissolve entirely when warmed. After saturation, a portion of the solution was removed through a pipette closed with a plug of glass wool and, after being weighed, was analyzed as follows: The solution was diluted with cold water, acidified with hydrochloric acid, and treated with hydrogen sulphide. Mercuric sulphide was filtered on a Gooch crucible, dried at 100°, and weighed. The filtrate was evaporated and the residue weighed as caesium chloride. The composition of the residue could then be calculated, and this was done except at the caesium end where the solutions contained a very large excess of caesium chloride. In this case it was found more accurate to analyze the residue. For this analysis the residue was dried as quickly as possible between filter-papers and analyzed by the method already given.

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[1] Am. J. Sci., 44, 221 (1892).

The results are in Table I. Column I. gives the number of the experiment; Columns II. and III., the parts by weight of caesium chloride and mercuric chloride, respectively, in 100 parts by weight of solution; Columns IV. and V., the percentage of caesium chloride and mercuric chloride in the residue; Column VI., the salts present in the residue. The results are separated into groups, each group representing (1) varying composition of the residue and constant composition of solution, where a mixture of two salts is present, or (2) constant composition of the residue and varying composition of solution, showing a pure salt. The results in the latter class, where a pure salt is present, are italicized:

Table I.—Solubility of Caesium and Mercuric Chlorides at 25°.

I.	II.	III.	IV.	V.	VI.
	CsCl in solution.	$HgCl_2$ in solution.	CsCl in residue.	$HgCl_2$ in residue.	Residue contains
1	*65.61*	*0*	*100*	*0*	CsCl
2	65.71	0.22	95.11	4.89	CsCl and Cs_3HgCl_5
3	65.86	0.21	70.12	29.88	" " "
4	*62.36*	*0.32*	*66.43*	*33.57*	Cs_3HgCl_5
5	*57.01*	*0.64*	*65.96*	*34.04*	"
6	*52.35*	*1.23*	*65.46*	*34.54*	"
7	51.17	1.45	62.86	37.14	Cs_3HgCl_5 and Cs_2HgCl_4
8	51.01	1.43	59.80	40.20	" " "
9	*49.30*	*1.49*	*56.21*	*43.79*	Cs_2HgCl_4
10	*45.95*	*1.69*	*55.47*	*44.53*	"
11	45.45	1.78	48.31	51.69	Cs_2HgCl_4 and $CsHgCl_3$
12	44.99	1.69	39.77	60.23	" " "

Table I.—Solubility of Caesium and Mercuric Chlorides at 25° (*Continued*).

I.	II. CsCl in solution.	III. $HgCl_2$ in solution.	IV. CsCl in residue.	V. $HgCl_2$ in residue.	VI. Residue contains
13	*38.63*	*1.32*	*37.85*	*62.15*	$CsHgCl_3$
14	*27.17*	*0.84*	*37.20*	*62.80*	"
15	*17.03*	*0.51*	*37.60*	*62.40*	"
16	*3.92*	*0.27*	*37.60*	*62.40*	"
17	*1.53*	*0.42*	*37.66*	*62.34*	"
18	0.63	2.66	36.81	63.19	$CsHgCl_3$ and $CsHg_2Cl_5$
19	0.59	2.62	30.99	69.01	" " "
20	*0.49*	*2.91*	*23.43*	*76.57*	$CsHg_2Cl_5$
21	*0.40*	*3.78*	*23.55*	*76.44*	"
22	0.43	4.62	20.46	79.54	$CsHg_2Cl_5$ and $CsHg_5Cl_{11}$
23	0.45	4.65	15.97	84.03	" " "
24	*0.41*	*4.68*	*11.30*	*88.70*	$CsHg_5Cl_{11}$
25	*0.25*	*5.65*	*10.84*	*89.16*	"
26	0.19	7.14	10.62	89.38	$CsHg_5Cl_{11}$ and $HgCl_2$
27	0.20	7.10	9.57	91.43	" " "
28	0.19	7.10	4.93	95.07	" " "
29	0.18	7.06	0.95	99.05	" " "
30	0.17	7.06	0.28	99.72	" " "
31	*0.09*	*7.02*	*0*	*100.0*	$HgCl_2$
32	*0*	*6.90*	*0*	*100.0*	"

Excluding the pure single salts, there are five groups where the residue is very nearly constant in each group, corresponding to five double salts. Table II. gives the calculated percentage of caesium chloride in the five double salts described by Wells. Underneath, the average percentage of caesium chloride in the above residues of each group, corresponding to a double salt, is given :

Table II.

	Cs_3HgCl_5.	Cs_2HgCl_4.	$CsHgCl_3$.	$CsHg_2Cl_5$.	$CsHg_5Cl_{11}$.
CsCl (calculated)	65.10	55.43	38.34	23.72	11.06
CsCl (found)	65.95	55.84	37.58	23.49	11.07

The results in Table II. show conclusively that the salts found were the same as those described by Wells. The possibility of the formation of other stable salts is excluded, as the differences in composition of the solutions and residues from group to group are but slight.

The results of Table I. have been plotted in Fig. I. The total percentage of dissolved salts has been chosen as ordinate

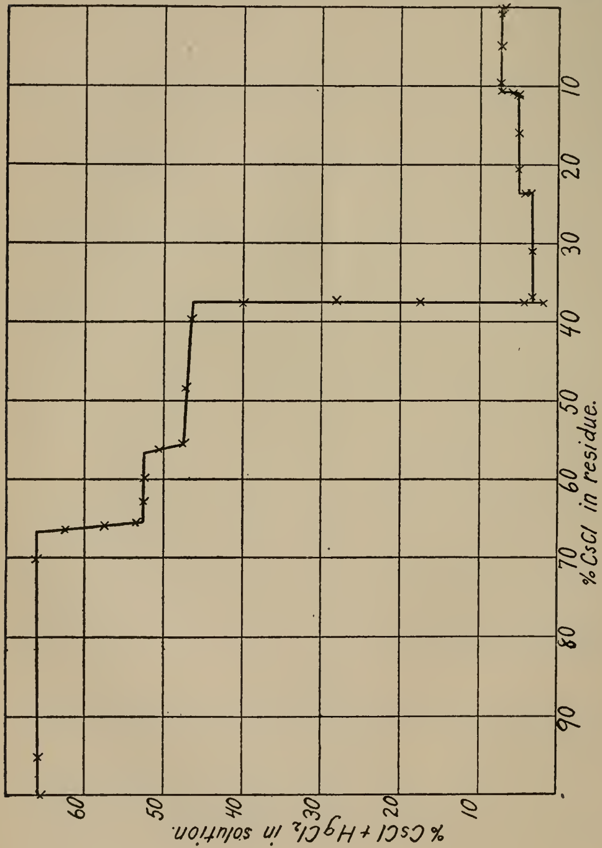

Fig. I.

and the percentage of caesium chloride in the residue as abscissa. The five lines running nearly vertically show nearly constant composition of the residue and variable solubility, corresponding to the five double salts, while each horizontal line represents a mixture of two salts with constant solubility.

Referring back to Table I., it will be noticed in Experiments 13 to 17 where the 1 : 1 salt is present that the amount of mercuric chloride in solution at first diminishes and then increases. The increase is but slight but continues in Experiments 18 and 19, where the 1 : 1 salt is mixed with the 1 : 2 salt. This irregularity would indicate a change in the double salt, but the composition of the residue remains constant. It was noticed by Wells[1] that the 1 : 1 salt occurs in two different crystalline modifications, one form crystallizing in cubes at the caesium end of the series, and the other in orthorhombic crystals at the mercury end. From the results in the table it is evident that the isometric crystals were present in Experiments 13 to 15, and the orthorhombic form in Experiment 17, and possibly in Experiment 16. A change of the crystalline form of a substance is usually associated with a change in temperature, there being but one temperature where both forms are stable. Above and below this temperature only one form can exist. In the present case, at constant temperature, both forms can exist in equilibrium only under one definite set of solubility conditions. Nearer the mercury end the orthorhombic form is stable, while at the caesium end of the series only the isometric form can exist. This conclusion is supported by the phase rule. In case both forms of the double salt were present, there would be four phases in the system, consisting of the two solids, solution and vapor, and three components. The system is thus monovariant. If the temperature be chosen as variable, the concentration of the solution will adjust itself and cannot be varied independently. When one phase disappears the system becomes divariant, and besides the temperature the concentration of the solution may be varied.

The corresponding double bromide, $CsHgBr_3$, is also dimorphous,[1] the two forms corresponding to those of the double chloride, and caesium lead bromide, $CsPbBr_3$, occurs in orange-colored and in colorless crystals.[2] In both these cases the two forms can occur at a given temperature, but the relative proportion of the two salts in solution determines which form is stable. Only when the dissolved salts are present in one definite proportion for a given temperature could both salts be stable together. The compound $CsCl_2I$ is also dimorphous[3] and similar influences appear to affect the crystalline form.

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[1] *Loc. cit.*

Summary.

The results in this article may be summarized as follows:

1. The solubility method of determining double salts, which was devised in the preceding article, has been applied to the double caesium and mercuric chlorides.
2. The five double salts described by Wells were detected and it was shown that no others formed at 25°.
3. The occurrence of two crystalline forms of a double salt at any one temperature was discussed, with examples.

New Haven, Conn., June, 1903.

THE SOLUBILITY-CURVE OF SODIUM TETRABORATE.

By D. W. Horn and Elizabeth M. Van Wagener.

The following paper is based on volumetric analyses of saturated solutions of borax, prepared from both supersaturated and unsaturated solutions, at a number of temperatures between 0° and 100°.

The well-defined, crystalline hydrates of sodium tetraborate have been known for a long time. The one, the decahydrate, $Na_2B_4O_7 + 10H_2O$, as "ordinary," "monoclinic," or "prismatic borax,"[4] and the other the pentahydrate, $Na_2B_4O_7 + 5H_2O$, as "octahedral borax."[5] These hydrates can be obtained from the same solution,[1] and in the solid form the decahydrate passes into the pentahydrate when it is heated.[2] From these facts an irregularity in the solubility-curve of sodium tetraborate is to be expected, for, repeatedly, experiment has shown that a change in the degree of hydration of a salt and a change in the direction of the solubility-curve of that salt (in water as a solvent) are interdependent.[3]

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[1] Wells: Am. J. Sci., **44**, 228 (1892).

[2] Walden: *Ibid.*, **45**, 128 (1893).

[3] Wells: *Ibid.*, **43**, 26 (1892).

[4] Known to early chemists; composition determined 1747 by Baron; used by Berzelius in determining atomic weight of boron.

[5] Discovered by Payen, 1829; Jsb., **8**, 171; Ding. polytech. J., **26**, 231.

According to the data from the measurements of the tension of water-vapor over borax, the temperature at which the transition of the decahydrate into the pentahydrate is complete is 60°.[4] An irregularity should occur in the solubility-curve at the point corresponding to this temperature. However, when the solubility of sodium tetraborate, as determined by Poggiale,[5] is represented in graphic form, the resulting curve undergoes no sudden change in direction throughout its course. In fact it is quite similar (see figure) to that of potassium chlorate,[6] of which no hydrates are known. Since no irregularity occurs, the curve and the corresponding behavior of the system must be considered exceptional, or the data must be assumed to be insufficient or erroneous.

Consideration of Poggiale's method does not lead one to expect great errors, but small ones would be difficult to avoid. Assuming that the errors are not great and that an irregularity at 60° would appear in the curve had enough determinations of solubility at temperatures near 60° been made, the curve is still exceptional and remarkable in that, though it is a compound curve, its two parts have so nearly the same direction and curvature as to form a continuous curve when joined together. In this respect the curve is unlike the larger number of those of salts having more than one hydrate within the same limits of temperature as the curve is plotted. Interpreted in accordance with the accepted ideas, this must mean that, except about 60°, the two different hydrates of sodium tetraborate approximate quite nearly to having the same heat of solution in its saturated solution. Our knowledge of the act of solution does not contradict the possibility of this, but our knowledge of a large number of other cases in point[1] warrants us in not expecting two entirely different substances to be exactly alike in this one property.

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[1] Gernez, 1874: Compt. rend., **78**, 68; Payen, 1843: Jsb., **22**, 147; Ann. chim. phys., [3], 8, 353; Arzruni, 1876: Jsb., 1876, p. 224; Pogg. Ann., **158**, 250.

[2] Lesceour, 1896: Ann. chim. phys. [7], **9**, 545.

[3] Ostwald: "Solutions" (tr. by Muïr), p. 75.

[4] The idea that 56° is the lower temperature limit for the existence of the pentahydrate probably originated in Payen's statement that when borax is dissolved in boiling water until the specific gravity of the solution becomes 1.246, the pentahydrate separates, on cooling, between 79° and 56°; and below 56°, the decahydrate. This temperature limit in a solution of one definite concentration is quite a different thing from the lowest temperature at which the pentahydrate can exist in equilibrium with its saturated solution. In fact, Gernez has shown that the pentahydrate crystallizes spontaneously from the proper supersaturated solutions at temperatures as low as 8°.

Lesceour's measurements show that at ordinary temperatures the pure decahydrate is stable, not having over it a measurable tension of water-vapor. With rising temperature the tension rises quite rapidly until 60° is reached, when it falls again below the measurable limit. Evidently at 60° the decahydrate ceases to exist. At this temperature the new hydrate formed is stable. Lesceour proved it to be the pentahydrate.

[5] Ann. chim. phys. [3], 8, 467 (1843).

[6] Etard: Compt. rend., **108**, 177 (1889).

As a result of these considerations, we have determined the solubility of sodium tetraborate with the view of testing the sufficiency and accuracy of the data given by Poggiale. His method consisted in evaporating saturated solutions of borax to dryness and weighing the residues after complete dehydration. Troublesome frothing accompanies this procedure, and his practice was to puncture the films in the froth with a glass point to release the imprisoned steam. Unless the temperature is carefully regulated, the salt is often thrown out with considerable force and the crucible, in which the experiment is being carried out, broken. We adopted a method that avoids evaporations to dryness. We have determined the sodium tetraborate in weighed quantities of the saturated solutions by titration (after dilution) with standard acid, using methyl orange as indicator.

The following table contains the averages of our analyses. For comparison, Poggiale's data are also given. The numbers represent the solubility expressed as the number of grams of sodium tetraborate (anhydrous borax) dissolved by 100 grams of water. The figures in the column marked "U" were obtained by analyses of saturated solutions prepared from unsaturated ones, an excess of the salt remaining in contact with the solution after saturation ; the figures in the column marked "S," by analyses of saturated solutions prepared from supersaturated ones. The supersaturated solutions were filtered beforehand and the experiment so conducted as to insure crystallization at or very near the temperature at which the solubility was desired.

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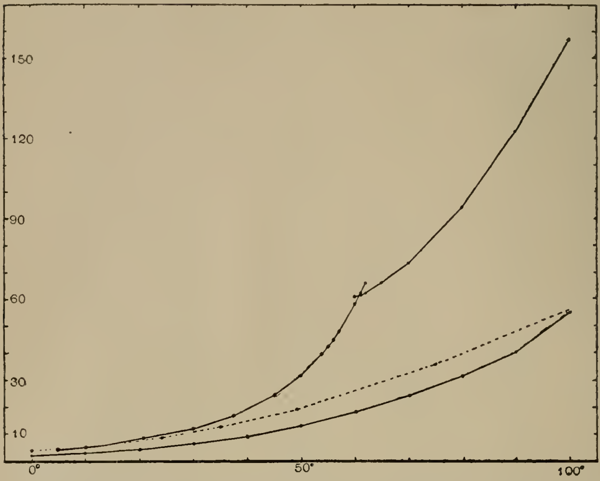
[1] Ztschr. phys. Chem., **5**, 198 (1890); Compt. rend., **98**, 993, 1276, 1432 (1884); **104**, 1614 (1887); **106**, 206, 740 (1888); Ann. chim. phys. [5], **30**, 411 (1883); J. Chem. Soc. (London), Feb., 1903 (barium acetate); and many other cases.

Temperature, C.	U.	S.	Average.	Poggiale's data.
0°				1.5
5°	1.3	1.4	1.3	
10°		1.6	1.6	2.4
20°				4.0
21°.5	2.8	2.8	2.8	
30°	4.0	3.9	3.9	6.0
37°.5	5.6	5.7	5.6	
40°				8.8
45°	8.1	8.1	8.1	
50°	10.4	10.6	10.5	12.9
54°	13.3	13.3	13.3	
55°	14.1	14.3	14.2	
56°	15.0	15.0	15.0	
57°	15.9	16.0	16.0	
60°	19.4	20.3		18.1
61°	20.7	20.4		
62°	22.0	20.7		
65°	22.0	21.9	22.0	
70°	24.5	24.4	24.4	24.2
80°	31.3	31.5	31.4	31.2
90°	40.7	41.0	40.8	40.1
100°	52.2	52.5	52.3	55.2

The relations between the data obtained at temperatures from 60° to 65° are different from those in other cases. The solubility as determined in solutions made from unsaturated solutions does not increase when the temperature is raised from 62° to 65°, and the increase in solubility for each degree from 60° to 62° is of a much smaller order than that for each degree from 54° to 57°. At 60° there is a considerable difference in the solubility depending on whether the experiment was begun with an unsaturated or a supersaturated solution, but the general rule that a greater value is gotten when a supersaturated solution is used for the preparation of the saturated solution holds good. At 61° and 62°, however, there is a reversal of this relation. The curve offers an interpretation for these results.



Lower curve, Poggiale's curve for sodium biborate; dotted curve, curve for potassium chlorate; upper curve, new curve for sodium biborate. In the upper curve the ordinates have each been changed to a different value to bring out more clearly the relations; ordinate = 3 × solubility.

We believe we have here to deal with meta-stability in the two hydrates. That of the decahydrate is the better defined. The values for the point on its curve at 62° were, after two and three hours, respectively, 22.02 and 21.92. On the other hand, the values for the point on the curve of the pentahydrate at 60° were 20.29 and 20.15 after two hours, and 19.80 and 19.79 after three hours. We believe this fall in solubility to be due to a transition (but partial, after three hours) of the pentahydrate into the decahydrate. At 61°, however, the pentahydrate is stable, the values for the point on its curve at this temperature being, after two and three hours, respectively, 20.48 and 20.31.

There is no evidence to be found in this curve, nor in the measurements of Lesceour, pointing to the existence of the hexahydrate, $Na_2B_4O_7 + 6H_2O$, described by Biechi,[1] as an incrustation at the Tuscan lagoons.

Details of Experiments.

In this work we used a water-bath of the type used and described by A. A. Noyes,[2] the shaft being turned by a small hot-air engine. Iron burette-clamps were so arranged on the shaft that two bottles of about 200 cc. capacity each could be firmly and quickly attached to it, and as quickly removed from it. The bottles were closed with rubber stoppers, well tied in. A thermometer with a long scale of about 115° was used. By constant attention and the use of hot and cold water and an extra burner it was possible to keep the temperature of the water in the bath constant within $\pm 0^\circ.1$. Each experiment lasted from four and a half to six hours. Two hours after the temperature had been adjusted and the shaft with bottles attached set in motion, the bottles were removed from the clamps on the shaft, the fastenings on the stoppers and the stoppers themselves loosened, and the bottles (loosely stoppered) fastened at the sides of the bath until the liquid in them was clear, all suspended matter having settled. This required from one-half to one and one-half hours, depending on the elevation of the temperature. When clear, specimens of the solutions were taken for analysis, the bottles closed, returned to the shaft, agitated for one hour more, and specimens taken again just as before. Two hours were sufficient for the point of saturation to be reached. The agitation for a third hour did not change the value for the solubility.

Some of the saturated solution was permitted to flow out from the bottle in such a way as to rinse its neck and lip, before the specimens for analysis were poured from it. The specimens were poured directly from the bottle into weighing-tubes provided with glass stoppers, the weight of each with its stopper having been determined just prior to the experiment. The stoppers were closed at once to prevent loss by evaporation, and when cold the tubes and contents were weighed and transferred to beakers containing hot water, in which all salt that had crystallized out dissolved. When the contents of the beakers were cold they were titrated with standard sulphuric acid, using methyl orange as indicator.

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[1] Am. J. Sci., [2], 17, 129; 19, 120; Jsb., 1854, p. 867.

[2] Ztschr. phys. Chem., 9, 606 (1892).

The unsaturated solutions were made by putting the decahydrate in contact with water, in quantities but little more than sufficient to saturate the water. The supersaturated solutions were made at temperatures about 10° above that of the corresponding experiment, and were filtered through a hot funnel into the bottle, which was immersed in a water-bath at the same temperature as that at which the solution had been made. The bottle was tightly stoppered before it was removed from this bath, and then transferred quickly to the large (solubility) bath, the temperature of which was from 1° to 2° higher than that at which the solubility was to be determined. When the bottles had been attached to the shaft and it had been started in motion, the temperature of the water of the bath was quickly reduced to that desired for the experiment by the cautious addition of cold water. In this way it was assured that crystallization took place at or very near the temperature at which the solubility was being determined.

The borax used was "refined" borax recrystallized from water till its solution showed no trace of $\overset{=}{SO_4}$ or $\overset{-}{Cl}$ when properly tested. The sulphuric acid was approximately N/5, and had been standardized by pure potassium tetroxalate and by pure borax, the standardizations being made by two different persons and checking up quite closely with each other.[1]

CHEMICAL LABORATORY,
BRYN MAWR COLLEGE,
June 1, 1903.

REVIEWS.

THE MEDICAL STUDENT'S MANUAL OF CHEMISTRY. By R. A. WITTHAUS, A.M., M.D., Professor of Chemistry, Physics, and Toxicology in Cornell University Medical College, New York City. Fifth edition. New York: William Wood & Co. 1902. pp. 678.

The edition has about the same scope as the previous one. It is intended to be used by medical students as a manual for inorganic, organic, and physiological chemistry. The part on organic chemistry has been in great part rewritten and somewhat extended. Covering as it does so much ground it is well-nigh impossible to present the material in a perfectly satisfactory way within the space allotted.

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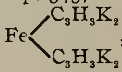
[1] Standardized by tetroxalate, 1 cc. contained 0.009577 gram of H_2SO_4; by borax, cc. contained 0.009584 gram H_2SO_4.

In the section on organic chemistry, more could perhaps be gained by omitting the description of many compounds that have at present no medical bearing, and paying more attention to the methods of determining the structure of a few typical compounds and thus conveying a clearer idea of what is meant by structural formulas. The latter 117 pages are devoted to physiological chemistry. The part dealing with the enzymes is entirely too brief when it is remembered that the book is intended for medical students, and it has not kept pace with the recent work in this field. For instance, the old distinction between formed and unformed ferments has hardly a place in a modern text-book and has been of little more than historical interest since Buchner's isolation of zymase in 1897. There is no justification for referring to the catalytic activity of enzymes as "false fermentations" (p. 243). In many places the style is not very clear and the meaning involved. A few errors have crept into the text, such as on p. 345, the formula for potassium ferrocyanide is given as  $Fe\begin{cases}C_3H_3K_2\\C_3H_3K_2\end{cases}$, etc.

Throughout the book especial emphasis is placed upon those substances of toxicological interest and on the reactions used in toxicology. The great development of the chemical aspect of the medical sciences in recent years renders it the more urgent that the chemical training of the medical student be more comprehensive and fundamental in character, and attempts to teach inorganic, organic, physiological, and clinical chemistry from a single book should be discouraged. Such attempts must necessarily be barren of results, and can only retard the growth of the chemical aspect of medicine.

A. S. L.

Determination of Radicles in Carbon Compounds. By Dr. H. Meyer, Docent and Adjunct of the Imperial and Royal German University, Prague. Translated by J. Bishop Tingle, Ph.D., F.C.S., Professor of Chemistry at Illinois College, Jacksonville, Illinois. Second edition, rewritten. 12mo. pp. xii + 162. New York: John Wiley & Sons. 1903.

The first edition of this book was reviewed in this Journal[1] soon after its appearance. Its usefulness "has been shown by the comparatively quick exhaustion of the first edition. The present issue has been thoroughly revised by Dr. Meyer and the writer, the whole work has been reset, and more than 20 per cent of new matter has been added, including several figures." Several new methods have been given, especially for the determination of alkyls, carbonyl, and the nitroso and methylene groups. It is believed that the book in its present form will prove even more generally useful than the first edition. C. E. W.

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[1] This Journal, 23, 451 (1900).

DER STICKSTOFF UND SEINE WICHTIGSTEN VERBINDUNGEN. By DR. LEOPOLD SPIEGEL, Privatdocent an der Universität Berlin. Braunschweig: Friedrich Vieweg und Sohn. 1903. 909 Seiten. Geheftet, 20 Mark; gebunden, 22 Mark.

This book is intended to bring together in convenient form an account of the more important compounds of the element nitrogen in order to facilitate the work of those who would otherwise be obliged to search through many journals and books to get a clear idea of the general relationships of their own particular field to the entire group of nitrogen compounds. It is intended to play the part for these that "Beilstein" does for the carbon compounds. The references to the literature are given as foot-notes, and the constants in tables that follow the text proper, in which the methods of preparation and other information are set forth. Thus, there are 18 pages of text devoted to the amines, imines, acid amides, amidines, and similar compounds. Following this are 79 pages of tables in which are given the names, formulas, melting- and boiling-points, and specific gravities of these substances. Sixteen pages of tables with similar information are given to the alkaloids, and the names of their discoverers and the sources from which they are obtained are also stated.

Among other general subjects the following are discussed: Nitrogen, the halides, oxides, sulphides, and hydrides of nitrogen, the nitrides, the cyanogen derivatives, nitrogen in closed rings, the alkaloids, the proteids, analytical methods, etc. The book is well printed, its arrangement is good, and it should prove of great value to all chemists, in spite of one or two minor points in which an improvement might be suggested. C. E. W.

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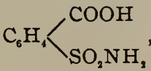
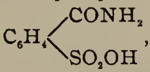
CHEMICAL JOURNAL

A COMPARATIVE STUDY OF ORTHOSULPHAMINEBENZOIC ACID AND ORTHOCARBAMINEBENZENESULPHONIC ACID.[1]

By Francis Daniel Wilson.

As methods are available for the preparation of orthosulphaminebenzoic acid,  $C_6H_4\left\langle\begin{matrix}COOH\\SO_2NH_2\end{matrix}\right.$, and of orthocarbaminebenzenesulphonic acid,  $C_6H_4\left\langle\begin{matrix}CONH_2\\SO_2OH\end{matrix}\right.$, and neither acid has been studied with especial care, Professor Remsen suggested that I should prepare them in considerable quantity and make a comparative study of them.

Preparation of Orthosulphaminebenzoic Acid.

This acid was first prepared by W. A. Noyes[2] by oxidizing orthotoluenesulphonamide with potassium ferricyanide. He described it as being easily soluble in alcohol and ether and quite readily in cold water. He obtained it in two different forms—fine needles and large prisms, which appeared to belong to the monoclinic system. He states that, when rapidly heated, the acid melts at 165° to 167°, but that, when slowly heated, it melts at 153° to 155°.

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[1] From the author's dissertation submitted, June, 1899, to the Board of University Studies of the Johns Hopkins University, in conformity with the requirements for the degree of Doctor of Philosophy. The investigation was undertaken at the suggestion of Professor Remsen and carried out under his guidance.

[2] This Journal, 8, 176.

The acid can be readily prepared by heating benzoic sulphinide with sodium hydroxide. The sulphinide was purified by the method suggested by Pope,[1] which consists in crystallizing the sulphinide from acetone. The sulphinide is more soluble in hot than in cold acetone. The parasulphaminebenzoic acid, which is sometimes found in benzoic sulphinide as an impurity, is insoluble in acetone. This being the case, it is an easy matter to separate the two substances. The sulphinide used in the following experiments contained scarcely a trace of parasulphaminebenzoic acid, even before it was treated with acetone. One hundred grams of the sulphinide required about 460 grams of acetone.

When the benzoic sulphinide is dissolved in hot acetone, a white, crystalline mass is deposited immediately upon cooling, but if the sulphinide is dissolved in cold acetone and the solution is allowed to evaporate spontaneously, large, colorless rhombohedrons are deposited, some of which are several millimeters in length.

It was found that, when the benzoic sulphinide is treated with sodium hydroxide under the following conditions, the orthosulphaminebenzoic acid is produced in nearly a quantitative yield: Twenty grams of pure benzoic sulphinide are added to a caustic soda solution, prepared by dissolving 15 grams of sodium hydroxide in 500 cc. of water. This solution was evaporated on a water-bath until the sweet taste of the sulphinide could no longer be detected. The solution was allowed to cool and then filtered. The acid was precipitated by means of hydrochloric acid. If the solution is stirred vigorously, after the addition of hydrochloric acid, the acid is precipitated at once in fine crystals. If allowed to stand over night without disturbance, large monoclinic crystals are deposited. After filtering, the acid was dissolved in alcohol, from which it crystallized in large, transparent rhombohedrons.

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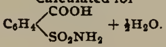
[1] J. Chem. Soc., 67, 985.

The acid, when heated slowly, melted at 152°; when heated rapidly, it melted at 159° C (uncorrected). It is quite soluble in alcohol and water. Some of the acid in a small boat was placed in a glass tube with a diameter of about 15 mm. One end of the tube was connected with a bottle containing a small quantity of sulphuric acid. The other end was connected with a cylinder which contained calcium chloride. By connecting this apparatus with a filter-pump, a current of dry air could be drawn through the tube. If the air was allowed to pass rapidly through the tube, the acid was decomposed when heated to about 128°. A white sublimate, which was very sweet, collected on the wall of the tube. If the current of air was shut off, the acid decomposed at 135° and white, transparent needles of pure benzoic sulphinide collected on the wall of the tube. Some of the needles were from 10 to 12 mm. in length. The acid contains no water of crystallization.

The acid crystallizes in white, opaque needles, if the solution is allowed to stand at least one week before crystallization takes place. The needles melt at 152°. The needles are more soluble in water than the plates. This form of the acid contains water of crystallization. Below 100° it lost just 0.5 molecule of water.

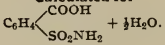
	Calculated for  $C_6H_4{<}^{COOH}_{SO_2NH_2} + \frac{1}{2}H_2O$.	Found.
H_2O	4.29	4.28

When dissolved in alcohol, the needles crystallize from the solution in plates which melt at 152°. The needles decomposed when heated to about 115°, and a white sublimate collected on the walls of the tube. The sublimate was very sweet.

Ten grams of benzoic sulphinide were added to a caustic soda solution, which was prepared by dissolving 20 grams of caustic soda in 250 cc. of water. The solution was treated in the same way as the previous solution. After treating the solution with hydrochloric acid, if it is allowed to stand over night, the acid crystallizes out in the form of needles. These proportions give nearly a quantitative yield of the acid in the form of needles.

A careful examination of the needles showed that they agreed in every respect with the needles obtained by the recrystallization of the plate acid from water. They melted at 152°. If the temperature is kept at 152° for a while, the acid is changed to a solid which melts at 215°. If heated in the apparatus previously described, the needles lose 0.5 molecule of water of crystallization below 100° C.

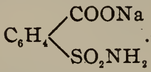
I. 0.3484 gram acid lost 0.0150 gram H_2O at 90°.
II. 0.2920 gram acid lost 0.0119 gram H_2O at 98°.

	Calculated for  $C_6H_4<{COOH \atop SO_2NH_2} + \frac{1}{2}H_2O$.	Found.	
		I.	II.
H_2O	4.29	4.30	4.11

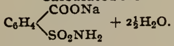
If a current of air was allowed to flow rapidly through the tube, the acid decomposed at 115° and was partially fused. When the current of air was cut off entirely, the acid decomposed at 145°. The acid was heated at this temperature for about six hours. During this time beautiful, transparent needles of pure benzoic sulphinide, some of which were several millimeters in length, collected on the walls of the tube. The needles were extremely sweet and melted at 223° to 224° (uncorrected). By taking proportions intermediate between the proportions used in the previous experiments (15 grams of sodium hydroxide with the same amount of benzoic sulphinide and water), a mixture is obtained which consists partly of the plate acid and partly of the needle acid. On account of the difference in solubility, they can easily be separated, the plates being less soluble than the needles.

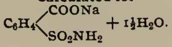
All of the salts of orthosulphaminebenzoic acid crystallize from water solution in well-formed crystals. All of them contain water of crystallization with the exception of the monosilver, potassium, and ammonium salts. Without exception, they all become sweet when they lose their water of crystallization.

All the salts decompose at a few degrees above the temperature at which they give off their water of crystallization.

Sodium Orthosulphaminebenzoate,  $C_6H_4<\begin{matrix}COONa\\SO_2NH_2\end{matrix}$.—This salt crystallizes from an exceedingly concentrated water solution in fine, silky needles. Only a few needles were obtained from a solution which was allowed to stand several weeks in a small test-tube. Even then a slight disturbance of the tube would cause the needles to redissolve. As a general rule, the salt is deposited as a white, amorphous mass. The salt becomes sweet by simply exposing it to the air for a short while. The salt was dried (with drying-paper) and analyzed at once. The percentage of sodium agreed with 1.5 molecules of water and the percentage of water of crystallization agreed with 2.5 molecules of water.

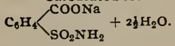
I. 0.2114 gram salt lost 0.0357 gram H_2O below 110°.
II. 0.2210 gram salt lost 0.0375 gram H_2O below 110°.
III. 0.2628 gram salt lost 0.0442 gram H_2O below 110°.

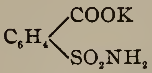
	Calculated for  $C_6H_4<\begin{matrix}COONa\\SO_2NH_2\end{matrix} + 2\tfrac{1}{2}H_2O$.	Fouud.		
		I.	II.	III.
H_2O	16.79	16.88	16.96	16.81

	Calculated for  $C_6H_4<\begin{matrix}COONa\\SO_2NH_2\end{matrix} + 1\tfrac{1}{2}H_2O$.	Found.		
		I.	II.	III.
Na	9.20	9.10	9.12	9.11

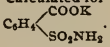
A few of the needles were obtained and a determination of the sodium agreed with 2.5 molecules of water.

I. 0.0174 gram salt gave 0.0046 gram Na_2SO_4.
II. 0.1945 gram salt gave 0.0546 gram Na_2SO_4

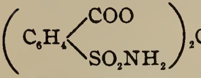
	Calculated for  $C_6H_4<\begin{matrix}COONa\\SO_2NH_2\end{matrix} + 2\tfrac{1}{2}H_2O$.	Found.	
		I.	II.
Na	8.58	8.62	8.58

Potassium Orthosulphaminebenzoate,  $C_6H_4<\begin{matrix}COOK\\SO_2NH_2\end{matrix}$.—This salt is extremely soluble in water; insoluble in methyl alcohol. It is deposited from a water solution as a white, amorphous mass. It crystallizes from a mixture of alcohol and water in large, transparent plates.

I. 0.1445 gram salt gave 0.0528 gram K_2SO_4.
II. 0.1265 gram salt gave 0.0457 gram K_2SO_4.

	Calculated for  $C_6H_4\left<\begin{matrix}COOK\\SO_2NH_2\end{matrix}\right.$.	Found. I.	II.
K	16.32	16.33	16.20

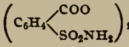
Calcium Orthosulphaminebenzoate,



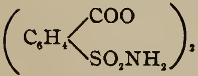
$\left(C_6H_4\left<\begin{matrix}COO\\SO_2NH_2\end{matrix}\right.\right)_2Ca + 2H_2O$.—This crystallizes from a water solution in well-formed, transparent crystals.

If crystallization takes place at once, well-formed crystals are obtained; but if the solution is allowed to stand several days, the salt is deposited as a white, crystalline mass.

I. 0.5475 gram salt lost 0.0414 gram H_2O below 140°.
II. 0.3776 gram salt lost 0.0277 gram H_2O below 140°.
I. 0.2114 gram salt gave 0.0598 gram $CaSO_4$.
II. 0.2926 gram salt gave 0.0829 gram $CaSO_4$.

	Calculated for  $\left(C_6H_4\left<\begin{matrix}COO\\SO_2NH_2\end{matrix}\right.\right)_2Ca + 2H_2O$.	Found. I.	II.
Ca	8.40	8.27	8.30
H_2O	7.56	7.57	7.33

Barium Orthosulphaminebenzoate,



$\left(C_6H_4\left<\begin{matrix}COO\\SO_2NH_2\end{matrix}\right.\right)_2 + 3H_2O$.—This salt is quite soluble in water and fairly soluble in alcohol. It crystallizes from a water solution in transparent plates, and sometimes it crystallizes from a water solution in needles in the form of rosettes. It crystallizes in needles from alcohol solution. It agrees in every respect with the salt prepared by W. A. Noyes[1] with the exception of the number of molecules of water of crystallization. Noyes prepared two salts, one with 2 molecules and another with 9 molecules of water of crystallization. This salt loses its water of crystallization when exposed to the air.

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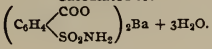
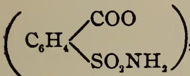
[1] *Loc. cit.*

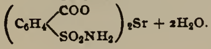
0.1823 gram salt lost 0.0171 gram H_2O below 150°.
I. 0.1214 gram salt gave 0.0483 gram $BaSO_4$.
II. 0.1076 gram salt gave 0.0426 gram $BaSO_4$.

	Calculated for	Found.	
	 $\left(C_6H_4\genfrac{}{}{0pt}{}{\diagup COO}{\diagdown SO_2NH_2}\right)_2Ba + 3H_2O.$	I.	II.
Ba	23.18	23.39	23.32
H_2O	9.14	9.14	....

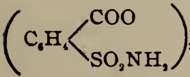
Strontium Orthosulphaminebenzoate,


$\left(C_6H_4\genfrac{}{}{0pt}{}{\diagup COO}{\diagdown SO_2NH_2}\right)_2Sr + 2H_2O$.—If the solution is allowed to evaporate spontaneously, this salt crystallizes in long, transparent, needle-like crystals, some of which are 3 or 4 mm. in length. The crystals remain transparent when exposed to the air.

I. 0.2151 gram salt lost 0.0150 gram H_2O below 140°.
I. 0.1385 gram salt gave 0.0486 gram $SrSO_4$.
II. 0.2231 gram salt gave 0.0783 gram $SrSO_4$.

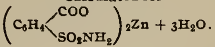
	Calculated for	Found.	
	 $\left(C_6H_4\genfrac{}{}{0pt}{}{\diagup COO}{\diagdown SO_2NH_2}\right)_2Sr + 2H_2O.$	I.	II.
Sr	16.71	16.71	16.67
H_2O	6.87	6.97	....

Zinc Orthosulphaminebenzoate,


$\left(C_6H_4\genfrac{}{}{0pt}{}{\diagup COO}{\diagdown SO_2NH_2}\right)_2Zn + 3H_2O$.—Two grams of the acid were dissolved in a sufficient quantity of water and pure zinc carbonate was added till the solution was neutral. The solution was evaporated to a slight extent, and allowed to stand in a desiccator over night. Short, opaque, needle-like crystals were deposited during the night. If the solution is allowed to evaporate spontaneously, after several days large, transparent, needle-like crystals are deposited, some of which were

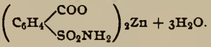
from 1 to 2 cm. in length. The crystals do not lose their transparency when exposed to the air. The salt is fairly soluble in water.

I. 0.0809 gram salt lost 0.0081 gram H_2O below 130°.
II. 0.0690 gram salt lost 0.0070 gram H_2O below 130°.
I. 0.0449 gram salt gave 0.0137 gram $ZnSO_4$.
II. 0.0621 gram salt save 0.0192 gram $ZnSO_4$.
III. 0.1476 gram salt gave 0.0456 gram $ZnSO_4$.

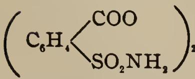
	Calculated for  $\left(C_6H_4\begin{matrix}COO\\SO_2NH_2\end{matrix}\right)_2Zn + 3H_2O$.	Found. I.	II.	III.
Zn	12.59	12.24	12.40	12.46
H_2O	10.39	10.01	10.15	....

The zinc salt was also prepared from the needle acid in order to compare it with the zinc salt prepared from the plate acid. The two salts resemble one another in every respect with one exception. The solution of the salt from the needle acid, when allowed to evaporate spontaneously, deposited large, opaque, needle-like crystals instead of the transparent needles obtained from the plate acid.

0.0652 gram salt gave 0.0201 gram $ZnSO_4$.
0.0138 gram salt lost 0.0138 gram H_2O below 150°.

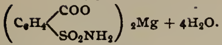
	Calculated for  $\left(C_6H_4\begin{matrix}COO\\SO_2NH_2\end{matrix}\right)_2Zn + 3H_2O$.	Found.
Zn	12.59	12.42
H_2O	10.39	10.64

Magnesium Orthosulphaminebenzoate,

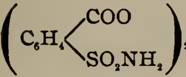


$\left(C_6H_4\begin{matrix}COO\\SO_2NH_2\end{matrix}\right)_2Mg + 4H_2O$.—This salt crystallizes in well-formed, transparent needles, which are deposited in the form of rosettes. It is extremely soluble in water.

I. 0.1850 gram salt lost 0.0270 gram below 175°.
II. 0.2458 gram salt lost 0.0355 gram H_2O below 175°.
I. 0.2129 gram salt gave 0.0519 gram $MgSO_4$.
II. 0.1726 gram salt gave 0.0425 gram $MgSO_4$.
III. 0.1416 gram salt gave 0.0341 gram $MgSO_4$.

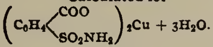
Calculated for  $\left(C_6H_4<\begin{smallmatrix}COO\\SO_2NH_2\end{smallmatrix}\right)_2Mg + 4H_2O$.	Found. I.	II.	III.
Mg	4.84	4.84	4.92	4.81
H_2O	14.52	14.59	14.42	....

Copper Orthosulphaminebenzoate,



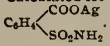
$\left(C_6H_4<\begin{smallmatrix}COO\\SO_2NH_2\end{smallmatrix}\right)_2Cu + 3H_2O$.—This forms large, blue, feathery needles, some of which are more than a centimeter in length. The salt is insoluble in alcohol and very difficultly soluble in water. The salt turned a deep-green color when it lost its water of crystallization.

I. 0.1369 gram salt lost 0.0144 gram H_2O below 170°.
II. 0.0895 gram salt lost 0.0095 gram H_2O below 170°.
III. 0.0951 gram salt lost 0.0085 gram H_2O below 170°.
I. 0.1684 gram salt gave 0.0209 gram CuO.
II. 0.3018 gram salt gave 0.0456 gram CuO.

	Calculated for  $\left(C_6H_4<\begin{smallmatrix}COO\\SO_2NH_2\end{smallmatrix}\right)_2Cu + 3H_2O$.	Found. I.	II.
Cu	12.23	12.41	12.32
H_2O	10.44	10.51	10.91

Monosilver Orthosulphaminebenzoate.—This was prepared by neutralizing 2 grams of the acid with ammonium hydroxide, and then boiling the solution until no odor of ammonia could be detected. Silver nitrate was added to the solution until no further precipitation took place. By allowing the solution to stand over night, fine, feathery needles of a light-gray color were deposited. The salt is soluble in hot water, but insoluble in cold water. It becomes dark when exposed to the light. It resembles, in every respect, the salt prepared by Noyes[1] by the same method.

I. 0.0875 gram salt gave 0.0307 gram Ag.
II. 0.1171 gram salt gave 0.0412 gram Ag.

	Calculated for  $C_6H_4<\begin{smallmatrix}COOAg\\SO_2NH_2\end{smallmatrix}$.	Found. I.	II.
Ag	35.06	35.08	35.17

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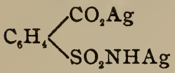
[1] *Loc. cit.*

Disilver Orthosulphaminebenzoate,



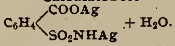
$C_6H_4<\begin{matrix}CO_2Ag\\SO_2NHAg\end{matrix}$ + H_2O.—This was prepared by neutralizing about 2 grams of acid with ammonium hydroxide and then adding about three-fourths as much ammonium hydroxide in excess as was required to neutralize the solution. Silver nitrate was added until no further precipitation took place. The salt was deposited as a white, amorphous mass, which dissolves in boiling hot water. By allowing the solution to stand over night, the salt separated out in the form of silver-colored leaflets, which became dark when exposed to the light. This salt is much less soluble in water than the mono-silver salt, and resembles in every respect, with one exception, the disilver salt prepared by Noyes[1] by treating the barium salt with silver nitrate. This salt contains 1 molecule of water of crystallization.

The salt was thoroughly dried and was allowed to remain wrapped in drying-paper for one week. It was then heated to 140° in the apparatus previously described. The current of air was cut off and water could be distinctly seen as it collected as drops in both ends of the tube. After losing its water, it becomes dark-brown in color.

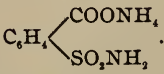
I. 0.1231 gram salt lost 0.0053 gram H_2O at 167°.

I. 0.1867 gram salt gave 0.0933 gram Ag.

II. 0.1097 gram salt gave 0.0549 gram Ag.

	Calculated for  $C_6H_4<\begin{matrix}COOAg\\SO_2NHAg\end{matrix}$ + H_2O.	Found. I.	 II.
Ag	49.88	49.97	50.04
H_2O	4.15	4.30	....

Ammonium Orthosulphaminebenzoate,



$C_6H_4<\begin{matrix}COONH_4\\SO_2NH_2\end{matrix}$.—This is quite soluble in water and crystallizes from a water solution in transparent plates. It contains no water of crystallization, but becomes very sweet when heated to 125°, and decomposes quite easily.

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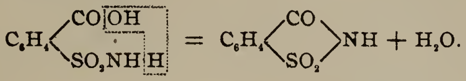
[1] *Loc. cit.*

Action of Phosphorus Oxychloride on the Sulphamine Acid.

Five grams of the acid were mixed with 5 grams of phosphorus oxychloride and heated on a water-bath for two hours. No chloride was formed. All of the acid was converted into benzoic sulphinide :



$$C_6H_4\left<\begin{matrix}CO\boxed{OH}\\SO_2NH\boxed{H}\end{matrix}\right. = C_6H_4\left<\begin{matrix}CO\\SO_2\end{matrix}\right>NH + H_2O.$$

Preparation of the Diamide, $C_6H_4\left<\begin{matrix}CONH_2\\SO_2NH_2\end{matrix}\right.$.

Ten grams of the acid were mixed with 6 grams of ammonium sulphocyanate. The mixture was heated, in a closed bath, for three days. During this time it was frequently stirred. As the acid is converted into benzoic sulphinide at quite a low temperature, the mixture was heated from 90° to 100° the first day, from 130° to 135° the second day, and from 150° to 160° the third day. The mass, which is of a light-brown color, is allowed to cool, when it becomes brittle. It is then pulverized and treated with boiling alcohol, in which it is soluble. After filtering, the solution is allowed to cool, when light-colored needles are deposited. Melting-point 263°.

Analyses gave the following results :

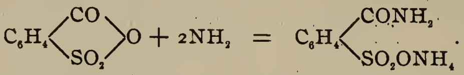
I. 0.1296 gram diamide gave 0.1528 gram $BaSO_4$.
I. 0.1565 gram diamide gave 0.0209 gram N.
II. 0.1413 gram diamide gave 0.0188 gram N.

	Calculated for $C_6H_4\left<\begin{matrix}CONH_2\\SO_2NH_2\end{matrix}\right.$.	Found. I.	Found. II.
S	16.00	16.20	....
N	14.00	13.35	13.27

I am indebted to Mr. C. E. Waters for the nitrogen determinations. He observed the fact that the ammonia is given off in two different stages. One portion of the ammonia was given off when the sodium hydroxide solution was dilute. After heating some time, the second portion was given off when the solution had become very concentrated.

Preparation of Orthocarbaminebenzenesulphonic Acid.

This acid was first prepared by Fahlberg and Barge[1] by the following method: Orthosulphobenzoic anhydride, when treated with ammonia, reacts according to this equation:



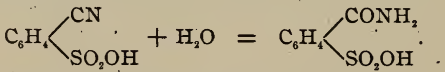
$$C_6H_4\left\langle\begin{matrix}CO\\SO_2\end{matrix}\right\rangle O + 2NH_2 = C_6H_4\left\langle\begin{matrix}CONH_2\\SO_2ONH_4\end{matrix}\right. .$$

The ammonium salt, when treated with silver nitrate, is easily converted into the silver salt. The free acid is obtained by treating the silver salt with sulphuric acid.

They describe the acid as crystallizing in thick, prismatic crystals, which are easily soluble in water and alcohol, and contain 1 molecule of water of crystallization. Melting-point 185° to 186° (uncorrected). By melting the acid with potassium hydroxide, ammonia is given off, but when simply heated no ammonia is given off.

The acid was prepared later by Jesurun[2] by heating orthocyanbenzenesulphone chloride with water or alcohol.

Karslake[3] also obtained the acid by hydrolysis of orthocyanbenzenesulphonic acid by means of dilute alkali:



$$C_6H_4\left\langle\begin{matrix}CN\\SO_2OH\end{matrix}\right. + H_2O = C_6H_4\left\langle\begin{matrix}CONH_2\\SO_2OH\end{matrix}\right. .$$

The potassium salt of the acid can be obtained in any desired quantity by treating the acid potassium salt of orthosulphobenzoic acid with ammonium sulphocyanate.[4]

The substances were mixed together in the proportion of 5 parts of acid potassium salt to 3 parts of ammonium sulphocyanate. The mixture was heated in a closed bath for three days at a temperature of from 180° to 200° C. During this time it was occasionally stirred. The mass, which is of a brown color, is allowed to cool, when it becomes a stiff cake. It is then finely pulverized and digested with boiling alcohol several times. The potassium salt of the acid, which is in the form of sandy crystals, was separated from the alcohol by filtering. The salt, when recrystallized from water, separates out in large, transparent plates.

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[1] Ber. d. chem. Ges., 22, 758.

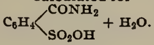
[2] *Ibid.*, 26, 2288.

[3] Dissertation, Johns Hopkins University (1896), page 18.

[4] English Patent, Newton & Son, February 23, 1895.

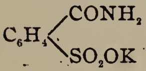
When the potassium salt is treated with silver nitrate in the proportion of their molecular weights, reaction takes place with the greatest ease with the formation of the silver salt of orthocarbaminebenzenesulphonic acid. The acid is obtained by treating the silver salt with hydrochloric acid. The acid crystallizes from a very concentrated water solution in large, thick, transparent crystals, which are quite soluble in alcohol. Melting-point 193° to 194° (uncorrected). The crystals remain transparent when exposed to the air. It does not become sweet when it loses its 1 molecule of water of crystallization, neither does it become sweet by continued heating. It decomposes when heated to 125°.

I. 0.2691 gram acid lost 0.0228 gram H_2O below 120°.
II. 0.2585 gram acid lost 0.0214 gram H_2O below 120°.

	Calculated for	Found.	
	 $C_6H_4<^{CONH_2}_{SO_2OH} + H_2O$.	I.	II.
H_2O	8.22	8.47	8.27

The salts of this acid do not crystallize as well as the salts of orthosulphaminebenzoic acid, but are much more soluble in water. Most of the salts contain water of crystallization but they do not become sweet when they lose their water, neither do they become sweet when they are decomposed.

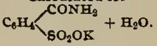
Potassium Orthocarbaminebenzenesulphonate,



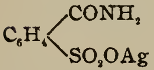
$C_6H_4<^{CONH_2}_{SO_2OK} + H_2O$.—This salt crystallizes from a water solution in large, transparent plates. It is quite soluble in water and in alcohol. It crystallizes from alcohol in needles. The salt is deliquescent. If the large, transparent crystals are placed in a beaker and covered with water, the moment they become warm a crackling sound can be distinctly heard some distance from the water-bath. The crystals become opaque and crumble to pieces. This phenomenon is doubtless due to the fact that the salt loses its water of crystallization very easily. In this instance it loses it under water.

A similar salt is described by Remsen and Karslake,[1] derived from cyanbenzenesulphonic acid, and by Sohon,[2] derived from the ammonium salt of benzaminesulphonic acid.

I. 0.3439 gram salt lost 0.0239 gram H_2O below 100°.
II. 0.5499 gram salt lost 0.0380 gram H_2O below 100°.
III. 0.4801 gram salt lost 0.0331 gram H_2O below 100°.
I. 0.4660 gram salt gave 0.1583 gram K_2SO_4.
II. 0.4904 gram salt gave 0.1657 gram K_2SO_4.
III. 0.4246 gram salt gave 0.1441 gram K_2SO_4.

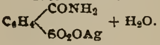
	Calculated for	Found.		
	 $C_6H_4{<}\genfrac{}{}{0pt}{}{CONH_2}{SO_2OK} + H_2O$.	I.	II.	III.
K	15.21	15.21	15.11	15.21
H_2O	7.00	6.94	6.91	6.89

Silver Orthocarbaminebenzenesulphonate,


$C_6H_4{<}\genfrac{}{}{0pt}{}{CONH_2}{SO_2OAg}$ + H_2O.—When the potassium salt of the carbamine acid in solution is treated with silver nitrate in the proportion of their molecular weights, the silver salt is formed. The salt which is fairly soluble in water crystallizes in large, monoclinic, transparent plates. It is decomposed when brought in contact with wet filter-paper and becomes dark when exposed to the light for any length of time.

This salt resembles in every respect the salt prepared by Fahlberg and Barge[3] by treating the ammonium salt of the carbamine acid with silver nitrate.

I. 0.3557 gram salt lost 0.0193 gram H_2O below 136°.
II. 0.4136 gram salt lost 0.0228 gram H_2O below 136°.
I. 0.2362 gram salt gave 0.0784 gram Ag.
II. 0.3681 gram salt gave 0.1215 gram Ag.

	Calculated for	Found.	
	 $C_6H_4{<}\genfrac{}{}{0pt}{}{CONH_2}{SO_2OAg} + H_2O$.	I.	II.
Ag	33.14	13.19	33.00
H_2O	5.52	5.45	5.51

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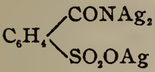
[1] This JOURNAL, 18, 825.

[2] *Ibid.*, 20, 270.

[3] Ber. d. chem. Ges., 22, 759.

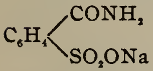
Trisilver Orthocarbaminebenzenesulphonate,



$C_6H_4{<}^{CONAg_2}_{SO_2OAg}$.—A small quantity of potassium orthocarbaminebenzenesulphonate was dissolved in water and 2 drops of ammonia were added to the solution. A hot solution of silver nitrate was added until no further precipitate was formed. The salt was deposited as a white, amorphous mass, which was insoluble in boiling water. The salt becomes dark when exposed to the light and is extremely stable. It was with the greatest difficulty that it was decomposed. Therefore, the following analysis cannot be reported with confidence:

	Calculated for $C_6H_4{<}^{CONAg_2}_{SO_2OAg}$.	Found,
Ag	62.07	62.56

Sodium Orthocarbaminebenzenesulphonate,



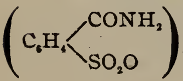
$C_6H_4{<}^{CONH_2}_{SO_2ONa} + 2H_2O$.—This salt was prepared by treating the silver salt with sodium chloride. It is quite soluble in water, from which solution it crystallizes in large, transparent plates, which belong to the monoclinic system.

This resembles in every respect the salt described by Remsen and Karslake.[1]

I. 0.1771 gram salt lost 0.0246 gram H_2O below 145°.
II. 0.1572 gram salt lost 0.0217 gram H_2O below 145°.
I. 0.1186 gram salt gave 0.0324 gram Na_2SO_4.
II. 0.0386 gram salt gave 0.0034 gram Na_2SO_4.

	Calculated for $C_6H_4{<}^{CONH_2}_{SO_2ONa} + 2H_2O$.	Found.	
		I.	II.
Na	8.88	8.85	8.80
H_2O	13.85	13.89	13.80

Barium Orthocarbaminebenzenesulphonate,



$\left(C_6H_4{<}^{CONH_2}_{SO_2O}\right)_2Ba + 2H_2O$.—This salt was prepared by treating the silver salt with hydrochloric acid and then adding pure barium carbonate to the point of neutralization. The salt crystallized in transparent plates from a very concentrated water solution.

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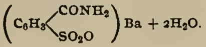
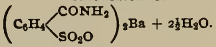
[1] *Loc. cit.*

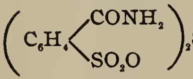
The percentage of water of crystallization agrees with 2 molecules of water. The percentage of barium agrees with 2.5 molecules of water. The following analyses were made of different portions of the salt prepared at different times:

I. 0.1787 gram salt lost 0.0114 gram H_2O below 175°.
II. 0.2194 gram salt lost 0.0138 gram H_2O below 175°.
I. 0.0887 gram salt gave 0.0357 gram $BaSO_4$.
II. 0.1584 gram salt gave 0.0637 gram $BaSO_4$.

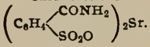
	Calculated for  $\left(C_6H_3\begin{array}{l}\diagup CONH_2\\ \diagdown SO_2O\end{array}\right)Ba + 2H_2O.$	Found. I.	II.
H_2O	6.28	6.37	6.28

	Calculated for  $\left(C_6H_4\begin{array}{l}\diagup CONH_2\\ \diagdown SO_2O\end{array}\right)_2Ba + 2\frac{1}{2}H_2O.$	Found. I.	II.
Ba	23.54	23.66	23.61

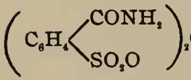
Strontium Orthocarbaminebenzenesulphonate,


$\left(C_6H_4\begin{array}{l}\diagup CONH_2\\ \diagdown SO_2O\end{array}\right)_2Sr.$—This salt was prepared just as the corresponding barium salt by using strontium carbonate. The salt separated out of an extremely concentrated water solution in small, transparent crystals with no definite form.

I. 0.2145 gram salt gave 0.0815 gram $SrSO_4$.
II. 0.2017 gram salt gave 0.0764 gram $SrSO_4$.

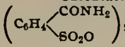
	Calculated for  $\left(C_6H_4\begin{array}{l}\diagup CONH_2\\ \diagdown SO_2O\end{array}\right)_2Sr.$	Found. I.	II.
Sr	17.95	18.08	18.04

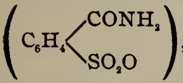
Calcium Orthocarbaminebenzenesulphonate,


$\left(C_6H_4\begin{array}{l}\diagup CONH_2\\ \diagdown SO_2O\end{array}\right)_2Ca + 2H_2O.$—This salt was prepared just as the corresponding strontium salt by using pure calcium

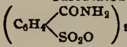
carbonate. The salt crystallized in large, transparent plates from a very concentrated water solution.

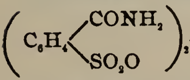
I. 0.1333 gram salt lost 0.0097 gram H_2O below 185°.
II. 0.1986 gram salt lost 0.0150 gram H_2O below 185°.
I. 0.1169 gram salt gave 0.0332 gram $CaSO_4$.
II. 0.1127 gram salt gave 0.0323 gram $CaSO_4$.

	Calculated for	Found.	
	 $\left(C_6H_4{<}\begin{matrix}CONH_2\\SO_2O\end{matrix}\right)_2Ca + 2H_2O$.	I.	II.
Ca	7.56	7.28	7.55
H_2O	8.40	8.29	8.43

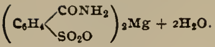
Zinc Orthocarbaminebenzenesulphonate,  $\left(C_6H_4{<}\begin{matrix}CONH_2\\SO_2O\end{matrix}\right)_2Zn + 3H_2O$.—This salt was prepared by treating the acid with pure zinc carbonate. The salt is deposited from a very concentrated water solution in the form of short, thick needles. It is efflorescent.

I. 0.2187 gram salt lost 0.0227 gram H_2O below 150°.
II. 0.2477 gram salt lost 0.0256 gram H_2O below 150°.
I. 0.0934 gram salt gave 0.0286 gram $ZnSO_4$.
II. 0.1022 gram salt gave 0.0320 gram $ZnSO_4$.

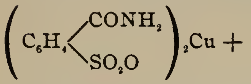
	Calculated for	Found.	
	 $\left(C_6H_4{<}\begin{matrix}CONH_2\\SO_2O\end{matrix}\right)_2 + 3H_2O$.	I.	II.
Zn	12.59	12.31	12.62
H_2O	10.39	10.37	10.34

Magnesium Carbaminebenzenesulphonate,  $\left(C_6H_4{<}\begin{matrix}CONH_2\\SO_2O\end{matrix}\right)_2 + 2H_2O$.—This salt was prepared just as the zinc salt by using pure magnesium carbonate. The salt separates out as a crystalline mass from a very concentrated water solution.

I. 0.1983 gram salt lost 0.0146 gram H_2O below 140°.
II. 0.2002 gram salt lost 0.0158 gram H_2O below 140°.
I. 0.1204 gram salt gave 0.0310 gram $MgSO_4$.
II. 0.1904 gram salt gave 0.0490 gram $MgSO_4$.

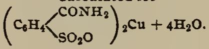
	Calculated for  $\left(C_6H_4\begin{matrix}\diagup CONH_2\\ \diagdown SO_2O\end{matrix}\right)_2Mg + 2H_2O.$	Found. I.	 II.
Mg	5.22	5.14	5.14
H_2O	7.82	7.36	7.89

Copper Orthocarbaminebenzenesulphonate,

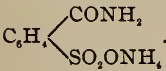


$\left(C_6H_4\begin{matrix}\diagup CONH_2\\ \diagdown SO_2O\end{matrix}\right)_2Cu + 4H_2O$.—This salt was prepared by boiling the acid with copper oxide on a water-bath. When allowed to cool the salt was deposited in beautiful, deep-blue plates. When the salt loses its water of crystallization it becomes gray. If a small quantity of water is added to the gray salt, it becomes light-blue.

I. 0.1761 gram salt lost 0.0240 gram H_2O below 200°.
II. 0.1760 gram salt lost 0.0240 gram H_2O below 200°.
I. 0.1083 gram salt gave 0.0127 gram CuO.
II. 0.0435 gram salt gave 0.0064 gram CuO.

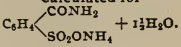
	Calculated for  $\left(C_6H_4\begin{matrix}\diagup CONH_2\\ \diagdown SO_2O\end{matrix}\right)_2Cu + 4H_2O.$	Found.	
Cu	11.86	11.72	11.72
H_2O	13.45	13.62	13.63

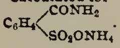
Ammonium Orthocarbaminebenzenesulphonate,



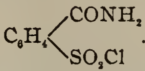
$C_6H_4\begin{matrix}\diagup CONH_2\\ \diagdown SO_2ONH_4\end{matrix}$.—This salt crystallizes from a concentrated water solution in large plates. One plate obtained was at least 2.5 cm. in length. After heating the salt up to 140° no sweet taste could be detected. It melts at 262° to 263° (uncorrected).

I. 0.1503 gram salt lost 0.0062 gram H_2O below 125°.
II. 0.1404 gram salt lost 0.0059 gram H_2O below 125°.
I. 0.1562 gram salt gave 0.1649 gram $BaSO_4$.

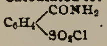
	Calculated for  $C_6H_4\begin{matrix}\diagup CONH_2\\ \diagdown SO_2ONH_4\end{matrix} + 1\frac{1}{2}H_2O.$	Found. I.	 II.
H_2O	3.96	4.12	4.20

	Calculated for  $C_6H_4\left<\begin{matrix}CONH_2\\SO_2ONH_4\end{matrix}\right.$.	Found.
S	14.67	14.46

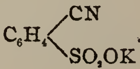
This salt was prepared by Fahlberg and Barge[1] and described as crystallizing from alcohol in white needles, which melt at 225° to 226°. Jesurun[2] describes it as crystallizing from water in granular crystals containing 1 molecule of water of crystallization. Remsen and Karslake[3] describe the salt as crystallizing from a water solution in thin, transparent needles, which contain no water of crystallization and which melt at 219° to 220° (uncorrected).

Preparation of the Chloride,  $C_6H_4\left<\begin{matrix}CONH_2\\SO_2Cl\end{matrix}\right.$.—Five grams of the potassium salt were mixed with 5 grams of phosphorus oxychloride in a small flask. The flask was attached to a return condenser, and then placed in a bath which contained boiling water. The mixture was heated for about half an hour. The white mass was pulverized in a mortar and treated with cold water. The orthocarbaminebenzenesulphone chloride, which remains in the form of a white, crystalline powder, insoluble in water, is filtered off. It was then thoroughly dried. It crystallized from chloroform in small, thick, opaque plates. Melting-point 63°.

0.1156 gram salt gave, by the Carius method, 0.0984 gram AgCl.

	Calculated for  $C_6H_4\left<\begin{matrix}CONH_2\\SO_2Cl\end{matrix}\right.$.	Found.
Cl	16.17	16.00

This experiment will be repeated, as it is somewhat doubtful whether the product obtained was the chloride of the carbamine acid.

Potassium Orthocyanbenzenesulphonate,  $C_6H_4\left<\begin{matrix}CN\\SO_2OK\end{matrix}\right.$.—

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[1] *Loc. cit.*

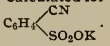
[2] *Loc. cit.*

[3] *Loc. cit.*

This was prepared by treating the potassium salt with phosphorus oxychloride, as in the previous experiment, only the mixture in this experiment was simply warmed in the water-bath. The whole of the potassium salt was converted into the cyan salt. It crystallizes from a moderately dilute water solution in small, transparent needles, radiating from a common center.

If the mixture of the potassium salt and phosphorus oxychloride is placed in a cold water-bath and then heated to the boiling temperature, the potassium salt will be partly converted into the chloride and partly into the cyan potassium salt.

This salt resembles in every respect the salt described by Remsen and Karslake,[1] derived from ammonium cyanbenzenesulphonate.

	Calculated for	Found.	
	 $C_6H_4\begin{cases}CN\\SO_2OK\end{cases}$.	I.	II.
K	17.67	17.67	17.71

A small portion of the chloride was placed in a beaker, which was then placed in a dish of cold water. The chloride was treated with a small quantity of an ordinary solution of ammonium hydroxide. The beaker was allowed to stand in the water for about three hours, the contents being stirred at frequent intervals.

It was then warmed on a water-bath for about half an hour. The solution was then filtered and a white, crystalline substance remained in the filter-paper. It was soluble only in boiling alcohol, from which solution it crystallized in small, opaque, monoclinic (?) plates. The substance did not melt when heated to the boiling-point of sulphuric acid. A sulphur determination was made by the Liebig method. Ammonia was given off when the substance was fused with potassium hydroxide, although not as freely as in the case of the diamide made from the sulphamine acid.

0.1203 gram substance gave 0.1506 gram $BaSO_4$.

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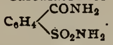
[1] *Loc. cit.*

	Calculated for  $C_6H_4<\begin{matrix}CONH_2\\SO_2NH_2\end{matrix}$	Found.
S	16.00	17.20

Possibly the substance was not thoroughly oxidized when fused with potassium hydroxide or else is not the diamide.

A FURTHER INVESTIGATION OF THE ACTION OF PHENOLS AND ALCOHOLS ON THE CHLORIDES OF PARANITROORTHOSULPHOBENZOIC ACID.[1]

By Victor John Chambers.

Action of Phenols.

The action of phenol upon the chlorides of orthosulphobenzoic acid has been studied. Remsen and Saunders[2] used the mixed chlorides and the symmetrical chloride, Remsen and McKee[3] both the symmetrical and the unsymmetrical chlorides.

In every case, a diphenyl ester and a red coloring-matter, supposed to be a sulphonphthalein, were obtained. Humphreys[4] repeated the work of Remsen and McKee and showed that, besides the two substances referred to, a third substance was obtained if the temperature was kept down. This proved to be the orthosulphone chloride of phenyl benzoate.

Less work has been done on the action of phenols upon the chlorides of paranitroorthosulphobenzoic acid. Henderson[5] tried the action of various phenols on the symmetrical chloride and obtained, with phenol and ortho- and paracresols, results analogous to those of Remsen and McKee.

It was thought best, therefore, to make a comparative study of the action of phenols upon the symmetrical and the unsymmetrical chloride.

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[1] From the author's dissertation submitted, June, 1901, to the Board of University Studies of the Johns Hopkins University, in conformity with the requirements for the degree of Doctor of Philosophy. The investigation was undertaken at the suggestion of Professor Remsen and carried out under his guidance.

[2] This Journal, **17**, 352.

[3] *Ibid.*, **18**, 794.

[4] *Ibid.*, **30**, 292.

[5] *Ibid.*, **25**, 1.

The method in general use was to mix a few grams of the chloride with slightly more than the required amount of the phenol, and to heat this mixture in a test-tube immersed in a bath of sulphuric acid. A large amount of the phthalein is formed in this way, which makes the product very difficult of purification. Humphreys showed that the Schotten-Baumann reaction could be applied to this case. He heated a mixture of the chloride and the phenol in a beaker until it liquefied. A cold, dilute solution of potassium hydroxide was then added and the oily mass stirred occasionally until it solidified. After washing and crystallization from glacial acetic acid, a very clean, pure product was obtained.

Both these methods were used by the author. In some cases where they did not give good results a third, or rather a modification of the second method, was used. This consisted in adding an alcoholic solution of potassium hydroxide to an alcoholic solution of the mixture of chloride and phenol. Potassium chloride separated and the product was obtained from the solution either by adding water slowly or by evaporating alcohol. In some cases, where the product was but slightly soluble in alcohol, it separated with the potassium chloride. After thorough washing with water, it was crystallized from glacial acetic acid.

Action of Phenol upon the Symmetrical Chloride.—Three grams of the symmetrical chloride were mixed with slightly more than the calculated amount of phenol and heated in a test-tube in the acid-bath to 135°. The results obtained were similar to those described by Henderson. The product was the diphenyl ester melting at 118° to 119°. Humphreys[1] obtained both the diphenyl ester and a small amount of the orthosulphone chloride of phenyl benzoate by a similar treatment of the symmetrical chloride of orthosulphobenzoic acid. The product in this case was examined for the corresponding orthosulphone chloride, but none was discovered.

A small portion of symmetrical chloride was mixed with an excess of phenol and heated in a beaker until it melted. Dilute solution of potassium hydroxide was then added and the oily mass stirred until it solidified and crumbled. The time required varies with the strength of the alkali solution and the temperature. If the solution is moderately strong and the mixture heated on a water-bath, the action is over in five minutes. The crumbly mass was filtered off, washed, and crystallized from glacial acetic acid or alcohol. Beautiful needles of the diphenyl ester were obtained. Melting-point 118°.

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[1] *Loc. cit.*

A small portion of the symmetrical chloride and the necessary amount of phenol were dissolved in alcohol. To this solution was added an alcoholic solution of potassium hydroxide until precipitation of potassium chloride had ceased. Impure diphenyl ester was obtained from the solution. After recrystallization from glacial acetic acid, it melted at 118°.

Conduct of the Diphenyl Ester towards Reagents.—Dilute potassium hydroxide completely saponifies the diphenyl ester. Alcohol does not change it even when boiled for hours.

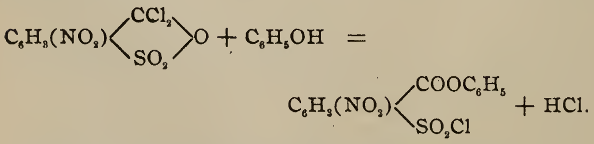
Action of Phenol upon the Unsymmetrical Chloride.—Three grams of the unsymmetrical chloride were mixed with a slight excess of phenol in a test-tube which was placed in a sulphuric acid-bath. Heat was applied and the temperature raised slowly to 135°, where it was kept for four hours. As soon as the substances melted, a red color was developed, which increased in depth until it became almost black. Hydrochloric acid commenced to come off at almost 100°. The rapidity of the evolution increased as the temperature rose, and decreased again after heating a short time at 135°. The black mass became somewhat viscous but did not harden on cooling. The cooled mass was treated with water, which dissolved much of the coloring-matter and caused the mass to harden.

The red solution so obtained was turned deep purple by the addition of an alkali. After as much of the coloring-matter had been extracted in this way as possible, the crumbly mass was decanted upon a filter and washed first with dilute alkali and then with hot water. The residue was recrystallized several times from glacial acetic acid. Light-brown, heavy needles were obtained which melted poorly at 145° to 147°.

These proved to be the paranitroorthosulphone chloride of phenyl benzoate.

The question arose whether any diphenyl ester was formed by this process. Humphreys,[1] working with the unsymmetrical chloride of orthosulphobenzoic acid, had obtained both products, the amount of each depending on the temperature. He found that, working at the lowest temperature at which the reaction would take place, he got a mixture containing, besides the phenyl ester chloride, a little of the diphenyl ester, while, if the temperature was raised, more diphenyl ester was found until, at a temperature just below the decomposition-point, practically only diphenyl ester was formed. This change is easily understood when it is borne in mind that the phenyl ester chloride itself reacts with phenol, forming the diphenyl ester. No diphenyl ester was found in the product of the reaction between phenol and the unsymmetrical chloride of paranitroorthosulphobenzoic acid. It will be shown later that the paranitroorthosulphone chloride of phenyl benzoate or, as it is often called, the phenyl ester chloride, does not react with phenol even when heated to the highest temperature short of decomposition.

A few grams of the unsymmetrical chloride were melted with an excess of phenol. The beaker was placed on ice, and to the oily mass was added a cold dilute solution of potassium hydroxide. The mass solidified very slowly. After washing and crystallizing from glacial acetic acid, pure crystals of phenyl ester chloride were obtained which melted at 146°. It is necessary to keep the temperature of the reaction low and the alkaline solution weak, for, if not, some or only diphenyl ester is obtained :



$$C_6H_3(NO_2)\left\langle\begin{matrix}CCl_2\\SO_2\end{matrix}\right\rangle O + C_6H_5OH = C_6H_3(NO_2)\left\langle\begin{matrix}COOC_6H_5\\SO_2Cl\end{matrix}\right. + HCl.$$

Analysis of the substance gave the following results :

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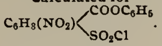
[1] *Loc. cit.*

0.2662 gram substance gave 0.4465 gram CO_2 and 0.0660 gram H_2O.

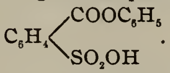
0.3147 gram substance gave 0.1308 gram AgCl.

0.2746 gram substance gave 0.1108 gram AgCl.

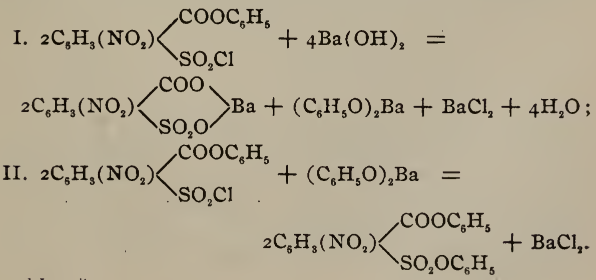
0.3560 gram substance gave 0.0146 gram N.

	Calculated for  $C_6H_3(NO_2)\left\langle\begin{matrix}COOC_6H_5\\SO_2Cl\end{matrix}\right.$.	Found.
C	45.68	45.76
H	2.74	2.34
Cl	10.37	10.28
N	4.10	4.10

Decompositions of the Paranitroorthosulphone Chloride of Phenyl Benzoate.—When boiled with dilute *hyarochloric acid*, the chloride is completely saponified giving free paranitroorthosulphobenzoic acid.

When boiled with *water*, it gives two products, the free acid and its monophenyl ester,  $C_6H_4\left\langle\begin{matrix}COOC_6H_5\\SO_2OH\end{matrix}\right.$. The ester was not obtained in pure condition but was identified by its crystalline form and an analysis.

Barium hydroxide gave results similar to those obtained by Humphreys.[1] The chloride was partly converted into the barium salt of paranitroorthosulphobenzoic acid and partly, apparently, into the diphenyl ester, the formation of which must be due to the action of the barium phenolate, first formed, upon some of the unchanged chloride:



$$\text{I.}\ 2C_6H_3(NO_2)\left\langle\begin{matrix}COOC_6H_5\\SO_2Cl\end{matrix}\right. + 4Ba(OH)_2 =$$

$$2C_6H_3(NO_2)\left\langle\begin{matrix}COO\\SO_2O\end{matrix}\right\rangle Ba + (C_6H_5O)_2Ba + BaCl_2 + 4H_2O;$$

$$\text{II.}\ 2C_6H_3(NO_2)\left\langle\begin{matrix}COOC_6H_5\\SO_2Cl\end{matrix}\right. + (C_6H_5O)_2Ba =$$

$$2C_6H_3(NO_2)\left\langle\begin{matrix}COOC_6H_5\\SO_2OC_6H_5\end{matrix}\right. + BaCl_2.$$

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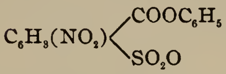
[1] *Loc. cit.*

Ammonia gives nitrobenzoic sulphinide and the diphenyl ester, whether used in dilute or concentrated form.

Aniline gives the anil described by Remsen and Gray.[1]

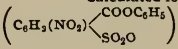
Alcohols convert the chloride into the monophenyl ester.

Barium Phenyl Paranitroorthosulphobenzoate,



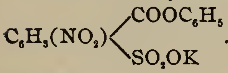
$\left(C_6H_3(NO_2)\left\langle\begin{array}{l}COOC_6H_5\\SO_2O\end{array}\right.\right)_2Ba + 5H_2O$.—This crystallizes from hot water in thin, lustrous plates. Another salt, containing probably 6 molecules of water, is formed when the hot solution is allowed to cool slowly. It has the form of white knobs.

0.2383 gram of the plates lost 0.024 gram H_2O at 170°.
0.2134 gram dried salt gave 0.0635 gram $BaSO_4$.

	Calculated for  $\left(C_6H_3(NO_2)\left\langle\begin{array}{l}COOC_6H_5\\SO_2O\end{array}\right.\right)_2Ba + 5H_2O$.	Found.
H_2O	10.34	10.41

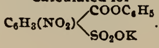
	Calculated for anhydrous salt.	Found.
Ba	17.58	17.51

Potassium Phenyl Paranitroorthosulphobenzoate,



$C_6H_3(NO_2)\left\langle\begin{array}{l}COOC_6H_5\\SO_2OK\end{array}\right.$.—This crystallizes in somewhat heavy needles.

0.2549 gram salt gave 0.0610 gram K_2SO_4.

	Calculated for  $C_6H_3(NO_2)\left\langle\begin{array}{l}COOC_6H_5\\SO_2OK\end{array}\right.$.	Found.
K	10.80	10.74

When the sulphone chloride is heated with phenol, even to the point at which decomposition begins, no diphenyl ester is formed. But when the two substances in alcoholic solution are treated with alcoholic potash, diphenyl ester is formed.

Action of Orthocresol upon the Symmetrical Chloride.—The results obtained by the heating together of these two substances were in perfect accord with those obtained by Henderson.[1]

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[1] This Journal, 19, 496.

Equal parts of the chloride and orthocresol were melted together. Dilute solution of potassium hydroxide was added and the mass stirred occasionally. The oily mass did not solidify perfectly even after two days' standing. It was dissolved in glacial acetic acid, from which solution rosettes of small crystals were obtained, melting at 95° to 97°. They were probably impure crystals of the unchanged chloride.

An alcoholic solution of potassium hydroxide was added slowly to an alcoholic solution of equal parts of the chloride and orthocresol. Granular crystals of potassium chloride at once separated. On allowing the alcoholic solution to evaporate, a crystalline mass was obtained that gave, upon recrystallization from glacial acetic acid, heavy needles melting at 90°.

This substance must be the same as was obtained in small quantity by Henderson by the fusion method. No analysis was made by him or the author, but there is little doubt that it is the diorthocresyl ester of paranitroorthosulphobenzoic acid.

Action of Orthocresol upon the Unsymmetrical Chloride.—The phenomena observed when these two substances were heated together were about the same as when the symmetrical chloride was used. Evolution of hydrochloric acid began a few degrees lower and the product did not become so hard on cooling. A much larger residue was left after washing which, when crystallized from glacial acetic acid, gave small, dark plates, melting poorly at 148°.

The Schotten-Baumann method gave better results. The mass hardened slowly and gave pure, white plates melting at 150° when crystallized from glacial acetic acid. These proved to be the paranitroorthosulphone chloride of orthocresylbenzoate.

0.3237 gram substance gave 0.5647 gram CO_2 and 0.0916 gram H_2O.

0.3456 gram substance gave 0.1365 gram AgCl.

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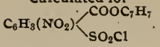
[1] *Loc. cit.*

	Calculated for  $C_6H_3(NO_2)\left\langle\begin{matrix}COOC_7H_7\\SO_2Cl\end{matrix}\right.$	Found.
C	47.26	47.57
H	2.81	3.29
Cl	9.96	9.74

Action of Paracresol upon the Symmetrical Chloride.—Equal parts of the symmetrical chloride and paracresol were melted together in a sulphuric acid-bath. A red color was developed quickly and deepened as the temperature rose. Hydrochloric acid came off at 100°. The temperature was raised to 115° and kept there for four hours, after which the mass was treated with cold water. It soon hardened, and after washing as before and recrystallizing from glacial acetic acid, short, thick needles were obtained which melted rather badly at 116°.

Equal parts of the symmetrical chloride and paracresol were melted together and treated with a 5 per cent solution of potassium hydroxide. The mass became oily, but hardened after two days. After washing and crystallizing from glacial acetic acid, fine, heavy needles were obtained, melting at 118°. The substance was the diparacresyl ester of paranitroorthosulphobenzoic acid obtained by Henderson[1] by the first of the two above processes.

Action of Paracresol upon the Unsymmetrical Chloride.—The reaction was carried on in the same way as with the symmetrical chloride. Hydrochloric acid was given off at about 100° and the mass turned from reddish-brown to black. The resultant mass, on washing and crystallization, gave small needles or prisms, melting at 152° (uncorrected). The product proved to be the paranitroorthosulphone chloride of paracresyl benzoate. The yield by this reaction is poor and hard to purify, yet it proved to be the only method by which it could be prepared.

The Schotten-Baumann method did not work smoothly in this case, the product being in every case the diparacresyl ester of paranitroorthosulphobenzoic acid. The reaction could not be made to stop half-way as it did with phenol and orthocresol.

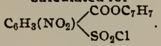
---

[1] *Loc. cit.*

That the product was the paranitroorthosulphone chloride of paracresyl benzoate was shown by the analysis :

0.2235 gram substance gave 0.3921 gram CO_2 and 0.0696 gram H_2O.

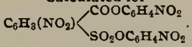
0.2571 gram substance gave 0.1005 gram AgCl.

	Calculated for  $C_6H_3(NO_2)\begin{matrix}COOC_7H_7\\SO_2Cl\end{matrix}$.	Found.
C	47.26	47.87
H	2.81	3.45
Cl	9.96	9.71

Action of Orthonitrophenol upon the Symmetrical Chloride.—Equal parts of the phenol and the chloride were melted together and heated with a dilute solution of potassium hydroxide. The oil so formed solidified after five hours' standing to a crumbly mass that, on washing and crystallization from glacial acetic acid, gave fine needles, melting sharply at 164°. This substance proved to be the dinitrophenylester of paranitroorthosulphobenzoic acid, as the following analysis shows :

0.1665 gram substance gave 0.2822 gram CO_2 and 0.0428 gram H_2O.

0.3058 gram substance gave 0.0261 gram N.

	Calculated for  $C_6H_3(NO_2)\begin{matrix}COOC_6H_4NO_2\\SO_2OC_6H_4NO_2\end{matrix}$.	Found.
C	46.62	46.25
H	2.05	2.81
N	8.59	8.52

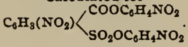
Action of Orthonitrophenol upon the Unsymmetrical Chloride.—When the chloride and phenol were heated together at 100°, the evolution of hydrochloric acid was slow. Even after heating to 125° for five hours, there was still some acid coming off. The mass was brown and was still an oil that hardened but partially on cooling. Caustic soda solution turned it to a crumbly mass after about two days' standing. The mass was washed and crystallized as usual. The product was an impure dinitrophenyl ester. The Schotten-Baumann method worked very smoothly, the result being rosettes of fine needles that melted sharply at 164°. The action here evidently led to the diorthonitrophenyl ester. All attempts to get the orthosulphone chloride by modifying the conditions of the experiment were useless.

Action of Paranitrophenol upon the Symmetrical Chloride.—The reaction in this case was more vigorous than that between the orthonitrophenol and the chloride. After heating in an acid-bath for five hours at 125°, a hard, black mass was obtained that dissolved in a solution of caustic soda, but was reprecipitated by acids as a flocculent, chocolate-colored mass. It was not further investigated. No ethereal salt was obtained.

The Schotten-Baumann method worked smoothly, giving rosettes of thick needles, melting at 152°.

The modified Schotten-Baumann method also gave a good yield and a very pure product.

0.1514 gram substance gave 0.2606 gram CO_2 and 0.0447 gram H_2O.

	Calculated for  $C_6H_3(NO_2)\langle{}^{COOC_6H_4NO_2}_{SO_2OC_6H_4NO_2}$.	Found.
C	46.62	46.93
H	2.05	....

Action of Paranitrophenol upon the Unsymmetrical Chloride.—The only difference noticeable between the action of the unsymmetrical chloride and that of the symmetrical was that the unsymmetrical acted a little more readily when fused with the nitrophenol in the acid-bath.

Action of Resorcinol upon the Symmetrical Chloride.—The addition of alcoholic potassium hydroxide solution to an alcoholic solution of resorcinol and chloride gave a flocculent precipitate at once. When the alkaline solution was added, a red color was developed at first, but disappeared on stirring, if the alkaline solution was not in excess. As soon as the color persisted, even after vigorously stirring, the precipitate was filtered off, washed thoroughly with water and alcohol, and dried.

The resulting, nearly colorless powder was practically insoluble in water, alcohol, glacial acetic acid, ether, chloroform, acetone, or ligroin. The very little that did dissolve in some of these solvents came out again in an amorphous condition. It was readily soluble in caustic alkalies, and was reprecipitated on acidifying. If, in the preparation of the substance, more alkali is added after the color has appeared, the precipitate dissolves, forming a reddish-green solution. This substance needs further investigation.

Action of Resorcinol upon the Unsymmetrical Chloride.—The action in this case was, in the main, the same as with the symmetrical chloride, the only difference being that the action took place a little more readily. The same hard mass was obtained which dissolved in alkaline solution and was reprecipitated by acids.

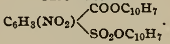
Action of Hydroquinol upon the Symmetrical Chloride.—When the modified Schotten-Baumann method was used, reaction took place as with resorcinol. The product had similar properties; in fact, what has been said about resorcinol can be repeated about the action of the chloride with hydroquinol.

Action of Hydroquinol upon the Unsymmetrical Chloride.—Hydrochloric acid commenced to come off at 120°, the melt becoming dark in color and viscous. After heating to 140° for four hours, a black mass was obtained which hardened on cooling, and acted like the mixture obtained with the other chloride.

In another experiment the temperature was kept at 125° for two hours. The mass darkened and thickened somewhat. When a solution of caustic soda was added, a part dissolved to a reddish-brown solution and the rest became oily, hardening only on standing. Nothing could be obtained from this mass but unchanged chloride.

Action of β-Naphthol upon the Symmetrical Chloride.—An alcoholic solution of potassium hydroxide was added to a similar solution of chloride and β-naphthol. A flocculent precipitate at once separated, which collected in a gummy mass on stirring. The addition of alkali was stopped as soon as the pale-brown color produced by it became permanent. The gummy mass became hard on standing. It was then filtered off, washed with water and dilute alkali, and crystallized from glacial acetic acid. Beautiful, white needles were obtained; melting-point 134°. Analysis showed it to be the di-β-naphthyl ester of paranitroorthosulphobenzoic acid.

0.2553 gram substance gave 0.6017 gram CO_2 and 0.0908 gram H_2O.

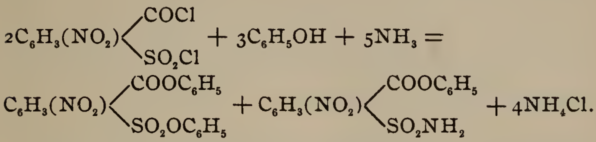
	Calculated for  $C_6H_3(NO_2)\begin{cases}COOC_{10}H_7\\SO_2OC_{10}H_7\end{cases}$.	Found.
C	64.91	64.30
K	3.42	3.97

Action of β-Naphthol upon the Unsymmetrical Chloride.—The results in this case were wholly unsatisfactory. The Schotten-Baumann reaction could not be used in alcoholic solution because alcohol acts upon this chloride.

Action of Paraminophenol upon the Unsymmetrical Chloride.—Equal parts of the phenol and chloride were heated in the acid-bath. No action took place until 125° was reached, when a slight evolution of hydrochloric acid was observed. The temperature was kept at 120° for four hours, during which time vapors of hydrochloric acid came off slowly and the mass became black and sticky, but did not at any time become a fluid. On cooling, a hard, shining, brittle mass was obtained which was insoluble in water but easily soluble in a warm solution of caustic soda. The solution thus formed was black. On acidifying, a chocolate-colored precipitate was formed. No ethereal salt was obtained.

The Action of Phenol in Solution in Ammonia upon the Two Chlorides of Paranitroorthosulphobenzoic Acid.—Two grams of the symmetrical chloride were melted with an equal quantity of phenol and covered with dilute ammonia. The oily mass hardened very slowly. After two days' standing, the mass was well washed, then dissolved in hot alcohol. On cooling, needle-shaped crystals separated that proved to be the diphenyl ester of paranitroorthosulphobenzoic acid. The alcoholic filtrate was allowed to evaporate at the room temperature and finally gave heavy prisms resembling the unchanged chloride, but melting at 135°. Analysis showed them to be phenyl paranitroorthosulphaminebenzoate.

The course of the experiment was varied in many ways but the result was always the same. The reaction is represented thus :



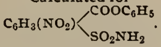
$$2C_6H_3(NO_2)\left\langle\begin{matrix}COCl\\SO_2Cl\end{matrix}\right. + 3C_6H_5OH + 5NH_3 =$$

$$C_6H_3(NO_2)\left\langle\begin{matrix}COOC_6H_5\\SO_2OC_6H_5\end{matrix}\right. + C_6H_3(NO_2)\left\langle\begin{matrix}COOC_6H_5\\SO_2NH_2\end{matrix}\right. + 4NH_4Cl.$$

0.3221 gram substance gave 0.5754 gram CO_2 and 0.0993 gram H_2O.

0.2366 gram substance gave 0.0204 gram N.

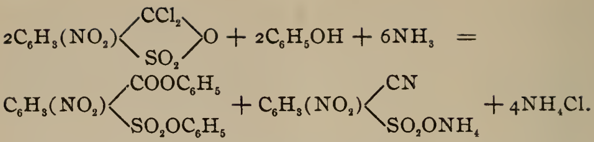
0.5172 gram substance gave 0.0445 gram N.

	Calculated for	Found.	
	 $C_6H_3(NO_2)\left\langle\begin{matrix}COOC_6H_5\\SO_2NH_2\end{matrix}\right.$.	I.	II.
C	48.45	48.71	....
H	3.10	3.42	....
N	8.69	8.62	8.61

The action of phenol and ammonia was tried also upon the unsymmetrical chloride. Equal parts of the unsymmetrical chloride and phenol were melted together and treated with dilute ammonia.

The oily mass soon solidified. It was then washed and dissolved in alcohol. Crystals of the diphenyl ester separated as in the previous experiment, but the alcoholic solution did not give any sulphonamide on evaporation. As Remsen and Gray[1] have shown that the action of ammonia upon the unsymmetrical chloride is to form the ammonium salt of paranitrocyanbenzenesulphonic acid, it is likely that some of this substance was also formed in this experiment.

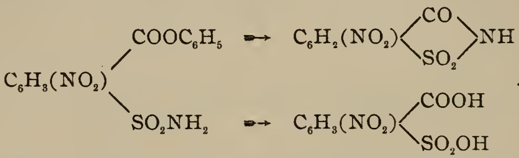
[1] *Loc. cit.*



$$2C_6H_3(NO_2)\left\langle\begin{array}{c}CCl_2\\SO_2\end{array}\right\rangle O + 2C_6H_5OH + 6NH_3 = C_6H_3(NO_2)\left\langle\begin{array}{l}COOC_6H_5\\SO_2OC_6H_5\end{array}\right. + C_6H_3(NO_2)\left\langle\begin{array}{l}CN\\SO_2ONH_4\end{array}\right. + 4NH_4Cl.$$

The action of caustic alkalies, ammonia, or water is the same as that of the same reagents upon the orthosulphonamide of phenyl benzoate.

A weak solution of potassium hydroxide causes the formation of the potassium salt of nitrobenzoic sulphinide. If the sulphonamide is heated a few moments with strong alkali, then acidulated, characteristic crystals of the acid potassium salt of paranitroorthosulphobenzoic acid are observed.



$$C_6H_3(NO_2)\left\langle\begin{array}{l}COOC_6H_5 \rightarrow C_6H_3(NO_2)\left\langle\begin{array}{c}CO\\SO_2\end{array}\right\rangle NH\\[2ex] SO_2NH_2 \rightarrow C_6H_3(NO_2)\left\langle\begin{array}{l}COOH\\SO_2OH\end{array}\right.\end{array}\right.$$

The action of ammonia was very slow. When the boiling was continued for five or more hours, the reaction was complete and nitrobenzoic sulphinide was formed.

The action of water was slower. This experiment was continued for five days without complete change taking place. There was some action, however, as the solution became gradually more bitter and gave more of a precipitate with bromine water. The common product of the action of weak alkalies, ammonia, and water upon the paranitroorthosulphonamide of phenyl benzoate is nitrobenzoic sulphinide.

Action of Alcohols upon the Chlorides.—Kastle[1] first studied the action of alcohols upon the chlorides of paranitroorthosulphobenzoic acid. He worked with the product of the reaction of phosphorus pentachloride upon the acid potassium salt of paranitroorthosulphobenzoic acid, a substance which was then supposed to be a chemical individual. He found that the substance dissolved readily in methyl alcohol with evolution of heat and, upon cooling, beautiful crystals were obtained.

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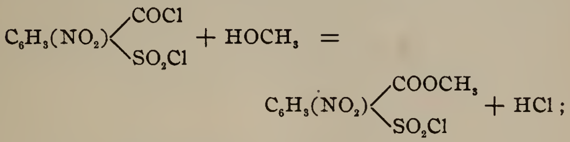
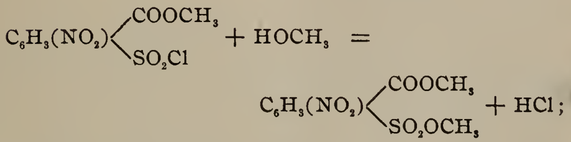
[1] *Loc. cit.*

This substance proved to be the paranitroorthosulphone chloride of methyl benzoate. If, however, the alcoholic solution of the chloride was boiled for a time, it became acid, and this acid was shown to be the acid methyl ester of paranitroorthosulphobenzoic acid. The sulphone chloride was also changed to the acid ester by boiling with alcohol.

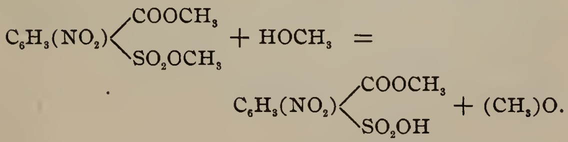
The following equations represent these reactions :

1.


$$C_6H_3(NO_2)\Big\langle\begin{matrix}COCl\\SO_2Cl\end{matrix} + HOCH_3 = C_6H_3(NO_2)\Big\langle\begin{matrix}COOCH_3\\SO_2Cl\end{matrix} + HCl;$$

2.


$$C_6H_3(NO_2)\Big\langle\begin{matrix}COOCH_3\\SO_2Cl\end{matrix} + HOCH_3 = C_6H_3(NO_2)\Big\langle\begin{matrix}COOCH_3\\SO_2OCH_3\end{matrix} + HCl;$$

3.


$$C_6H_3(NO_2)\Big\langle\begin{matrix}COOCH_3\\SO_2OCH_3\end{matrix} + HOCH_3 = C_6H_3(NO_2)\Big\langle\begin{matrix}COOCH_3\\SO_2OH\end{matrix} + (CH_3)O.$$

Henderson[1] has studied the action of alcohols upon the symmetrical chloride. He found that when that chloride was dissolved in methyl alcohol and then cooled, no sulphone chloride came out. Any substance that did separate proved to be the unchanged chloride. If the alcoholic solution was boiled for a time the acid methyl ester described by Kastle was obtained. Ethyl alcohol acted in an analogous way. He modified the conditions of the experiment in various ways, but failed entirely to get the sulphone chloride from the symmetrical chloride. A small quantity of the unsymmetrical chloride that he had in his possession did give, with ethyl alcohol, a substance melting at 68° and corresponding to the sulphone chloride described by Kastle.

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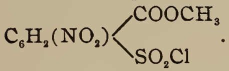
[1] *Loc. cit.*

It was thought best to study now the action of alcohols upon the unsymmetrical chloride to see if the results explained the formation of the sulphone chlorides from the mixed chlorides.

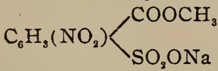
Action of Methyl Alcohol upon the Unsymmetrical Chloride.—A small portion of the chloride was added to a little methyl alcohol. It dissolved readily. On putting the solution on ice, there was a rapid separation of crystals. These were filtered off and recrystallized from a little methyl alcohol. Small, thick prisms were obtained, melting at 82°.[1] This substance is the paranitrosulphone chloride of methyl benzoate,



$$C_6H_2(NO_2)\left\langle\begin{matrix}COOCH_3\\SO_2Cl\end{matrix}\right. .$$

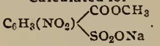
When the chloride is boiled with alcohol for a short time, an acid solution is obtained that does not become cloudy on the addition of water. The alcoholic solution evaporates to a syrup, which finally solidifies to a crystalline mass. The compound was identified by means of the following salts and proved to be monomethyl paranitroorthosulphobenzoate.

Sodium Methyl Paranitroorthosulphobenzoate,

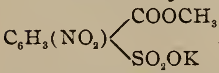


$C_6H_3(NO_2)\left\langle\begin{matrix}COOCH_3\\SO_2ONa\end{matrix}\right.$.—This crystallizes from a concentrated solution in transparent plates.

0.1955 gram substance, heated to 170°, lost 0.0003 gram.
0.1952 gram substance gave 0.0488 gram Na_2SO_4.

	Calculated for  $C_6H_3(NO_2)\left\langle\begin{matrix}COOCH_3\\SO_2ONa\end{matrix}\right.$.	Found.
Na	8.12	8.13

Potassium Methyl Paranitroorthosulphobenzoate,



$C_6H_3(NO_2)\left\langle\begin{matrix}COOCH_3\\SO_2OK\end{matrix}\right.$.—This is fairly soluble in cold water, from which it crystallizes in beautiful, iridescent plates.

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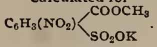
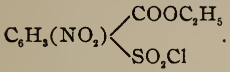
[1] Kastle: This JOURNAL, 11, 182.

I. 0.1238 gram substance gave 0.0370 gram K_2SO_4.
II. 0.1604 gram substance gave 0.0473 gram K_2SO_4.

	Calculated for  $C_6H_3(NO_2)\left\langle\begin{array}{l}COOCH_3\\SO_2OK\end{array}\right.$.	Found. I.	II.
K	13.18	13.39	13.21

Action of Ethyl Alcohol upon the Unsymmetrical Chloride.—This substance was made by dissolving the unsymmetrical chloride in ethyl alcohol and cooling the solution. Beautiful, white, heavy needles separated at once. On recrystallization from ethyl alcohol, they melted sharply at 68°. The substance is the paranitrosulphone chloride of ethyl benzoate,

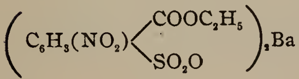


$$C_6H_3(NO_2)\left\langle\begin{array}{l}COOC_2H_5\\SO_2Cl\end{array}\right..$$

By boiling the unsymmetrical chloride with alcohol until a small portion dissolved in water to a clear solution, a very acid solution could be obtained which evaporated to a syrup without crystallizing. On long standing, however, this syrup did solidify to a crystalline mass.

The acid is also obtained by dissolving the unsymmetrical chloride in more alcohol than is necessary to keep the above sulphone chloride in solution, and allowing this solution to evaporate at the room temperature.

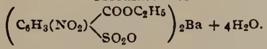
Barium Ethyl Paranitroorthosulphobenzoate,



$\left(C_6H_3(NO_2)\left\langle\begin{array}{l}COOC_2H_5\\SO_2O\end{array}\right.\right)_2Ba + 4H_2O$.—This salt crystallizes in long, white needles. It was recrystallized several times. The salt is very soluble in hot water, but only slightly in cold.

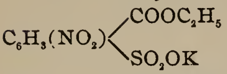
0.2549 gram substance lost, by heating to 170°, 0.0238 gram H_2O.

0.2311 gram substance gave 0.0786 gram $BaSO_4$.

	Calculated for  $\left(C_6H_3(NO_2)\left\langle\begin{array}{l}COOC_2H_5\\SO_2O\end{array}\right.\right)_2Ba + 4H_2O$.	Found.
H_2O	9.51	9.34

	Calculated for the dry salt.	Found.
Ba	20.00	20.02

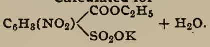
Potassium Ethyl Paranitroorthosulphobenzoate,


$C_6H_3(NO_2)\langle\begin{matrix}COOC_2H_5\\SO_2OK\end{matrix}$

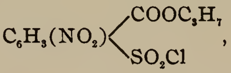
$C_6H_3(NO_2)\langle\begin{matrix}COOC_2H_5\\SO_2OK\end{matrix} + H_2O$.—This salt is very soluble in water and crystallizes from a concentrated solution in short, heavy prisms.

0.2763 gram substance lost, by heating to 170° C., 0.0150 gram H_2O.

0.2458 gram dried salt gave 0.0699 gram K_2SO_4.

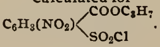
	Calculated for  $C_6H_3(NO_2)\langle\begin{matrix}COOC_2H_5\\SO_2OK\end{matrix} + H_2O$.	Found.
H_2O	5.42	5.43
	Calculated for dry salt.	Found.
K	12.59	12.75

Action of Propyl Alcohol upon the Unsymmetrical Chloride.—A portion of the unsymmetrical chloride was dissolved in warm propyl alcohol. Upon cooling, large, thin plates of the paranitrosulphone chloride of propyl benzoate,

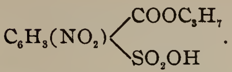

$$C_6H_3(NO_2)\langle\begin{matrix}COOC_3H_7\\SO_2Cl\end{matrix},$$

separated. After recrystallization from warm propyl alcohol, the substance melted at 76°.

I. 0.3273 gram substance gave 0.1523 gram AgCl.
II. 0.2743 gram substance gave 0.1276 gram AgCl.

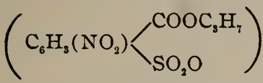
	Calculated for  $C_6H_3(NO_2)\langle\begin{matrix}COOC_3H_7\\SO_2Cl\end{matrix}$.	Found. I.	Found. II.
Cl	11.51	11.50	11.51

By boiling the unsymmetrical chloride with propyl alcohol in a flask, connected with a return condenser, until a solution was obtained that did not turn cloudy with water, then evaporating to a syrup and adding water, it gave a clear, very acid solution that decomposed carbonates readily. By the aid of the salts below described, the acid was shown to be the monopropyl ester of paranitroorthosulphobenzoic acid,



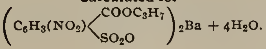
$$C_6H_3(NO_2)\left\langle\begin{matrix}COOC_3H_7\\SO_2OH\end{matrix}\right. .$$

Barium propyl paranitroorthosulphobenzoate,

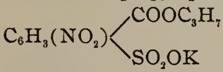


$\left(C_6H_3(NO_2)\left\langle\begin{matrix}COOC_3H_7\\SO_2O\end{matrix}\right.\right)_2Ba + 4H_2O$, crystallizes well from warm water in long needles with a somewhat greenish hue. The crystals are easily soluble in warm water, less so in cold. They contain 4 molecules of water of crystallization, which are driven off below 170°.

0.2337 gram substance lost 0.0219 gram on heating to 170°.
0.2118 gram of dried salt gave 0.0689 gram $BaSO_4$.

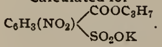
	Calculated for  $\left(C_6H_3(NO_2)\left\langle\begin{matrix}COOC_3H_7\\SO_2O\end{matrix}\right.\right)_2Ba + 4H_2O.$	Found.
H_2O	9.17	9.37
	Calculated for dry salt.	Found.
Ba	19.26	19.15

Potassium propyl paranitroorthosulphobenzoate,



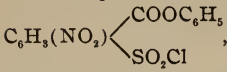
$C_6H_3(NO_2)\left\langle\begin{matrix}COOC_3H_7\\SO_2OK\end{matrix}\right.$, crystallizes from a concentrated solution in small, heavy needles. It is easily soluble in both hot and cold water.

0.1750 gram substance lost nothing on heating to 170°.
0.1750 gram substance gave 0.0471 gram K_2SO_4.

	Calculated for  $C_6H_3(NO_2)\left\langle\begin{matrix}COOC_3H_7\\SO_2OK\end{matrix}\right. .$	Found.
K	11.92	12.06

The results just described, taken with those of Henderson on the action of alcohols upon the symmetrical chloride, explain more fully the results obtained by Kastle. The sulphone chloride that he first obtained came from the unsymmetrical chloride, while the acid ester is seen to be the final product of the action of alcohols upon both chlorides.

Summary.

1. The paranitroorthosulphone chloride of phenyl benzoate,  $C_6H_3(NO_2)\begin{cases}COOC_6H_5\\SO_2Cl\end{cases}$, is formed by the action of phenol on the unsymmetrical chloride, but not from the symmetrical chloride. Ortho- and paracresol act in the same way.

2. The paranitroorthosulphone chloride of ethyl benzoate is formed by the action of ethyl alcohol upon the unsymmetrical chloride, but is not obtained from the symmetrical chloride. Methyl and propyl alcohols act in the same way. By further action of the alcohols, the chlorides are converted into the corresponding acids.

3. The paranitroorthosulphonamide of phenyl benzoate is formed by the action of phenol and ammonia upon the symmetrical chloride, but is not obtained from the unsymmetrical chloride.

4. Both chlorides, when treated with phenol in alkaline solution, give the diesters as the end-products. By modifying the conditions of the experiment, ester chlorides are obtained in the case of phenol and orthocresol.

Contributions from the Chemical Laboratory of the Massachusetts Institute of Technology.

XLII.—THE CONDENSATION OF CARBON TETRACHLORIDE WITH CHLORBENZENE BY MEANS OF THE FRIEDEL AND CRAFTS REACTION.

By James F. Norris and W. C. Twieg.

In a preliminary communication[1] from this laboratory, on the condensation of carbon tetrachloride with certain halogen derivatives of benzene by means of the Friedel and Crafts reaction, it was shown that when chlorbenzene reacts with carbon tetrachloride under these circumstances, but two benzene rings are joined to the methane carbon atom and, as a consequence, a ketone chloride is formed. As with benzene, however, under the same conditions, three halogen atoms are displaced and a quantitative yield of triphenylchlormethane is formed,[1] it seemed advisable to continue the study of this reaction. It was shown in the first paper that the product of the reaction, when chlorbenzene was used, could be isolated, after the decomposition of the aluminium addition-product, by distillation under reduced pressure. The substance proved to be an oil which had a constant boiling-point. It was decomposed when warmed with dilute alcohol, and, on cooling, 4,4′-dichlorbenzophenone was deposited in pure condition. The oil, on analysis, gave results agreeing with the formula $(ClC_6H_4)_2C.Cl_2$, and was accordingly considered to be 4,4′-dichlorbenzophenone chloride.

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[1] Norris and Green: This Journal, 26, 492.

When this oil was obtained by distilling the product of the reaction under diminished pressure, there was left a residue which varied in amount in different experiments. In order to isolate the substance contained in this residue in pure condition, if possible, the reaction was more fully studied, with the hope of obtaining trichlortriphenylchlormethane, the substance which would be formed if the reaction proceeded as in the case of benzene and carbon tetrachloride. This compound, as well as the ketone chloride formed, was required for investigations which are now being carried out in this laboratory.

New methods for the isolation of the reaction-products were studied and, as a consequence, it was discovered that the oil previously described as 4,4′-dichlorbenzophenone chloride consisted of a mixture of two isomers. The dipara-compound was present, but mixed with it was a quantity of an isomer, which was shown to have, in all probability, the structure of 2,4′-dichlorbenzophenone chloride.

The ketone chlorides could not be separated, as their boiling-points were very close together, and as they, apparently, formed a constant-boiling mixture. To effect the separation, the chlorides were first converted into the corresponding ketones. The dipara-compound was slightly soluble in cold alcohol and in cold ligroin, while the orthopara-compound was readily soluble in both solvents.

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[1] This JOURNAL, 25, 54.

A substance which was identical with the isomer of the dipara-ketone was prepared by the condensation of orthochlorbenzoyl chloride with chlorbenzene. It has been shown that when benzoyl chloride is condensed with chlorbenzene, the benzoyl group takes the position para to the halogen atom in the benzene ring. It follows, therefore, that the isomer has, in all probability, the orthopara-structure. In the first paper on this subject, the fact was mentioned that a small quantity of a compound was obtained which melted at 66° to 68°. This substance we have now shown to be the isomer of 4,4′-dichlorbenzophenone.

As it was found impossible to separate the original products of the reaction between carbon tetrachloride and chlorbenzene, the crude reaction-product, after decomposition with water to remove the aluminium chloride, was treated with concentrated sulphuric acid, in which it was slowly soluble with evolution of hydrogen chloride. When the acid was no longer given off, the product was poured into water. In this way the halogen atoms attached to the methane carbon atom were replaced by oxygen. The mixture so obtained could now be separated into its constituents. By treatment with ligroin, everything but the dipara-ketone was dissolved. By distilling the soluble portion under reduced pressure, the ortho-para-ketone was separated from a residue which could not be distilled. When a solution of the mixture in alcohol, after the removal of the dipara-ketone, was allowed to evaporate slowly, a mixture of the crystals of the orthoparadichlorketone and an oil was obtained. From the reactions, properties, and method of preparation of this oil, it was probably a third possible isomeric ketone—2,2′-dichlorbenzophenone. It could not be obtained in pure condition, as it decomposed when heated under a pressure of 18 mm. Trichlortriphenylchlormethane may have been formed in the reaction, but its presence was not discovered.

It is probable, therefore, that when carbon tetrachloride is condensed with chlorbenzene by the Friedel and Crafts reaction, but two chlorine atoms of the tetrachloride are displaced and that three dichlorbenzophenone chlorides are thus formed.

This result is of interest in connection with the results obtained with benzene where, under the same conditions, three chlorine atoms are removed and triphenylchlormethane is formed.

In one experiment a separation of the reaction-products was made as accurately as possible. From 60 grams of carbon tetrachloride there were obtained 25 grams of the dipara-ketone, 27 grams of the orthopara-compound, and 36 grams of the oil. In another experiment the mixture of the dipara- and orthoparadichlorbenzophenone chlorides, which distilled at a constant boiling-point, was converted into the corresponding ketones. Eighteen grams of the dipara- and 13 grams of the orthopara- compounds were obtained.

In view of the work which has been done on the condensation of chlorbenzene in the Friedel and Crafts reaction, the results are of interest, inasmuch as in the past it has been found that the para position is the one taken by the entering group almost to the exclusion of the ortho position.

The work on the condensation of paradichlorbenzene with carbon tetrachloride has been continued, as the ketone chloride produced is being used in another investigation. The method of carrying out the reaction has been so improved that the yield of 2,5,2′,5′-tetrachlorbenzophenone chloride has been increased to nearly four times that previously obtained.

EXPERIMENTAL.

A condensation of carbon tetrachloride was carried out as described in the paper referred to above, using 60 grams of carbon tetrachloride (1 molecule), 84 grams of chlorbenzene (2 molecules), 90 grams of aluminium chloride (1.75 molecules), and 300 cc. carbon bisulphide. Sixty grams of an oil boiling at 232° to 233°, at 25 mm. pressure, were obtained. This oil proved to be a mixture of the chlorides of 4,4′- and 2,4′-dichlorbenzophenones. The non-volatile residue weighed 15 grams. By increasing the amount of aluminium chloride to 120 grams, the yield was increased to 80 grams.

A portion of this distillate was decomposed by shaking with concentrated sulphuric acid. When all had passed into solution, the mixture was poured into water. The resulting ketones, after drying, were separated by warming them with ligroin. On cooling, nearly all the 4,4′-dichlorbenzophenone crystallized out. The soluble part was purified by repeated crystallization from dilute alcohol. Forty grams of the mixed chlorides gave 18 grams of the pure 4,4′-dichlorbenzophenone and 13 grams of the 2,4′-dichlorbenzophenone.

In another experiment the procedure was changed to that most favorable to the formation of a compound containing three benzene rings. Sixty grams of carbon tetrachloride (1 molecule), 120 grams of powdered aluminium chloride, and 126 grams of chlorbenzene (3 molecules) were allowed to react in the presence of 300 cc. of carbon bisulphide. After the mixture had stood over night, during which time a large quantity of hydrogen chloride was evolved, it was heated on a water-bath for a number of hours. After decomposition of the reaction-product by water, the organic part was extracted with carbon bisulphide, which was then removed by distillation. The residue was allowed to stand with concentrated sulphuric acid. When hydrogen chloride was no longer given off, the mixture was extracted with carbon bisulphide in order to remove the excess of chlorbenzene. As but 10 grams of an oil insoluble in sulphuric acid were obtained, and as only one-half of this proved to be chlorbenzene, it seems probable that more than 2 molecules of chlorbenzene had entered into reaction. No evidence of this, however, was obtained by a study of the reaction-product. The solution in sulphuric acid was poured into water. After the separation of the mixture from the dilute acid the former was treated with warm ligroin until the residue became crystalline. After standing some time, 22 grams of 4,4′-dichlorbenzophenone were left undissolved. This was purified by recrystallization from warm alcohol. The ligroin was separated from the part which had dissolved. An attempt was made to separate a small part of the residue into its constituents by crystallization. As a mixture of an oil and ill-defined crystals was obtained, the major part of the product was subjected to distillation at 23 mm. Under these circumstances, the 2,4′-dichlorbenzophenone distilled unchanged. On recrystallization, the distillate was found to contain a small amount of the dipara-compound. As a result of the experiment, 24 grams of 4,4′-dichlorbenzophenone and 27 grams of 2,4′-dichlorbenzophenone were obtained. The large residue could not be distilled or brought to crystallization.

Preparation of 2,4′-Dichlorbenzophenone from o-Chlorbenzoic Acid.—Ten grams of *o*-chlorbenzoic acid and 13 grams of phosphorus pentachloride were heated under a return condenser on a water-bath for several hours. On distillation, 6.5 grams of the acid chloride, boiling at 228°, were obtained. The product was dissolved in 100 cc. of carbon bisulphide, to which were added 4.5 grams of chlorbenzene and 5 grams of aluminium chloride. After standing a few hours, the mixture was heated on a water-bath for a short time. After the decomposition of the aluminium compound, the product was taken up in carbon bisulphide and treated with dilute alkali. One gram of *o*-chlorbenzoic acid was recovered. After removal of the solvent, the residue was taken up in alcohol. Upon slow evaporation, stout, white needles, which melted at 66° to 68°, separated. Finally a mixture of white needles and a red oil was left. The oil was removed from the crystals by filtration when the solvent had evaporated. The oil appeared to resemble the undistillable part of the reaction-product described above. The yield of the crystals was 4.35 grams. These proved to be identical with the low-melting ketone obtained from carbon tetrachloride. When recrystallized from alcohol, the pure compound was obtained as stout, colorless prisms, which melted at 66°.5 to 67°. A portion of this ketone obtained from the Friedel and Crafts reaction was found to boil at 214° to 215° at 22 mm. A determination of chlorine in the ketone gave 28.28 and 28.41 per cent, while the theory required 28.28 per cent. The compound is soluble in most organic solvents. It crystallizes best from ligroin or cold, dilute 60 to 75 per cent alcohol.

2,4′-Dichlorbenzophenone Chloride.—Seventeen grams of the ketone and 14 grams of phosphorus pentachloride were heated on the water-bath for a few hours. The mixture was then distilled under diminished pressure. The chloride distilled as a colorless, syrupy oil at 236°, at 34 mm. When redistilled, it boiled at 223° at 23 mm. The oil did not solidify in a freezing-mixture. It was soluble in most organic solvents and was readily converted into the corresponding ketone.

4,4′-Dichlorbenzophenone Chloride.—Twenty-seven grams of pure 4,4′-dichlorbenzophenone (the boiling-point of which was found to be 243° at 38 mm.) was heated with 23 grams of phosphorus pentachloride on an oil-bath, at 150° for one hour. On distillation, 28 grams of product were obtained. When treated with ligroin, in which the chloride is soluble, it was found that 5 grams of the ketone had distilled unchanged. Accordingly, a higher temperature was used in the next experiment.

Forty-four grams of the ketone were heated with 38 grams of phosphorus pentachloride at 170° to 180° for four hours. When distilled, 24.5 grams of the ketone chloride were obtained. A high-boiling residue was left. The action of the phosphorus pentachloride was evidently carried too far. When redistilled, the chloride boiled at 223° at 18 mm. The oily distillate soon changed to a mass of stout, prismatic crystals, which melted at 52° to 53°. The ketone chloride is readily soluble in ligroin, from which it crystallizes readily. When treated with dilute alcohol or with concentrated sulphuric acid, it is converted into 4,4′-dichlorbenzophenone.

2,5,2′,5′-Tetrachlorbenzophenone Chloride.—A study of the best conditions for the condensation of carbon tetrachloride with *p*-dichlorbenzene led to the following results: Ten grams of carbon tetrachloride, 20 grams of *p*-dichlorbenzene, 50 cc. of carbon bisulphide, and 20 grams of *powdered* aluminium chloride were heated on a steam-bath for three hours. The insoluble aluminium compound was washed with carbon bisulphide and then decomposed by water. The organic product was extracted with carbon bisulphide and the solution so obtained evaporated to a small bulk. On slow evaporation, the chloride of 2,5,2′,5′-tetrachlorbenzophenone was deposited in large, brilliant, colorless crystals. By treatment with a small quantity of ether the coloring-matter was removed. When the above proportions were used, 18 grams of the pure compound were obtained. The analysis and properties of the compound were given in the former paper.

BOSTON, MASS., July 10, 1903.

Preliminary Report from the Kent Chemical Laboratory of the University of Chicago.

THE "BECKMANN REARRANGEMENT." III.

STEREOISOMERIC CHLORIMIDO ACID ETHERS.

BY JULIUS STIEGLITZ AND RICHARD B. EARLE.

In two previous papers[1] on the "Beckmann rearrangement," one of us called attention to the importance of determining the rôle of the hydrogen atom, H*, when the acylhalogenamides, RCONH*Hal, are made to suffer a "Beckmann rearrangement" to amines and their derivatives (Hofmann's reaction) under the influence of alkalies. It was shown by Stieglitz and Slosson that no such rearrangement could be effected after the hydrogen atom was replaced by an alkyl or alphyl group with the production of the two possible isomeric series, the acylalkylhalogenamines, RCO(NR'Hal), and the halogenimidoesters, RC(OR')(NHal). The alkyl derivatives are comparatively stable compounds, a fact which is especially impressive in the case of the more interesting of the two series, the halogenimidoesters. They have the same constitution as the metal salts,[2] RC(OMe)(NHal), of the parent substance, salts which, as is well known, suffer the rearrangement with remarkable ease at rather low temperatures (0° to 30°). But methyl chlorimidometanitrobenzoate, for instance, may be heated to 140° without undergoing any change.

This remarkable stability of the ethers, which have the same constitution as the salts, seemed altogether incompatible[3] with the most generally accepted explanation of the "Beckmann rearrangement," that of Hoogewerff and van Dorp,[4] as a direct exchange of an alkyl group for a halogen atom caused by the greater affinity of nitrogen for carbon radicals than for halogens. On the basis of the newly proved constitution of the salts of the acylhalogenamides, Hantzsch[1] recently formulated the conception of Hoogewerff and van Dorp as follows:

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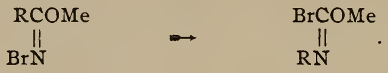
[1] Stieglitz: This JOURNAL, 18, 751 (1896); 29, 49 (1903); and also the investigations with E. E. Slosson: Ber. d. chem. Ges., 28, 3266 (1895); 34, 1613 (1901); This JOURNAL, 29, 289 (1903).

[2] Hantzsch: Ber. d. chem. Ges., 35, 228 (1902); Stieglitz and Ransom: *Ibid.*, 34, 1615 (1901) (footnote); This JOURNAL, 29, 64 (1903).

[3] Stieglitz: This JOURNAL, 29, 49 (1903).

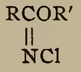
[4] Rec. trav. chim. Pays-Bas., 6, 373 (1887), etc.



$$\begin{array}{l}\mathrm{RCOMe}\\ \quad\| \\ \mathrm{BrN}\end{array} \longrightarrow \begin{array}{l}\mathrm{BrCOMe}\\ \quad\| \\ \mathrm{RN}\end{array}.$$

The alkali used in the reaction is supposed to be necessary only in order to produce the double bond between the carbon and the nitrogen atoms and thus to bring the alkyl group and the bromine atom into favorable proximity for an exchange of positions.

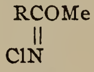
Our only hesitation in rejecting this interpretation absolutely on the basis of the proved stability of the corresponding alkyl ethers arose from the fact that these chlorimidoethers had been obtained by us only in one form, and it was still possible[2] that this one known form might belong to a stable *anti*-series, the rearranging salts to a *syn*-series of stereoisomers, as expressed in the following formulas:



$$\begin{array}{l}\mathrm{RCOR'}\\ \quad\| \\ \quad\mathrm{NCl}\end{array}$$

"*Anti.*"

and



$$\begin{array}{l}\mathrm{RCOMe}\\ \quad\| \\ \mathrm{ClN}\end{array}$$

"*Syn.*"

We have, therefore, continued our efforts to prepare stereoisomeric ethers in order to test experimentally this last possible objection to our argument against Hoogewerff and van Dorp's interpretation of the "Beckmann rearrangement." We believe that we have at length succeeded in isolating a pair of such stereoisomers, *viz.*, two methyl ethers of chlorimidometanitrobenzoic acid. These bodies represent, at the same time, the simplest case of *cis-trans* isomerism of nitrogen compounds as yet discovered. As is well known, such a form of stereoisomerism has hitherto been observed with any certainty only in the case of oximes, hydrazones, and some diazo compounds. In all of these cases the third bond of the doubly bound nitrogen atom carries some radical, *e. g.*, OH, NHC_6H_5; in no case, however, a single atom like that of chlorine, although, for theoretical reasons, earnest efforts have often been made to prepare such simple representatives of the type of stereoisomerism elaborated by Hantzsch and Werner. The new isomers form this long-missed link in their fruitful theory.

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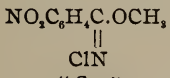
[1] Ber. d. chem. Ges., **35**, 3579 (1902).

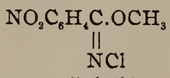
[2] Stieglitz: This JOURNAL, 18, 751 (1896); **29**, 55 (1903).

The isomers were discovered only a few weeks ago. But as our work is about to be interrupted for half a year, we feel obliged to publish our results at once in order to hold the field of work.[1] We have already been able to prove that the two ethers in question are identical as regards constitution and molecular weight, and we also have excluded experimentally the possibility of physical isomerism (crystal modifications). All possible forms of isomerism, excepting that of stereoisomerism, having thus been excluded, the two ethers must be space isomers. On the basis of the theory of Hantzsch and Werner, the relation would be that of *syn-* and *anti-*forms, *viz.*:



$$\begin{array}{c} NO_2C_6H_4C.OCH_3 \\ \| \\ ClN \end{array}$$

"*Syn.*"



$$\begin{array}{c} NO_2C_6H_4C.OCH_3 \\ \| \\ NCl \end{array}$$

"*Anti.*"

Although time and material were lacking for a complete examination of the chemical changes of the isomers, we have been able to show that both isomers are stable bodies which remain unchanged when warmed for some time to 80°, or even when heated a few minutes to 140°. Consequently, neither suffers a "Beckmann rearrangement" under the influence of heat. We have never observed, as yet, a change of one stereoisomer into the other. The absence of the tendency to rearrangement in both cases is not at all due then to any possible tendency of a reactive *syn*-form to go over into a more stable *anti*-form under the conditions which are used to rearrange the metal salts. Our observations up to the present, therefore, strengthen most decidedly our objections to the interpretation of the "Beckmann rearrangement" given by Hoogewerff and van Dorp and by Hantzsch, and favor the explanation of the reaction given by one of us.[1]

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[1] In the autumn the preparation of other stereoisomeric nitrogen halides will be attempted (the salts of the acylhalogenamides also exist possibly in two forms). The parent substances of the chlorimido ethers, the imido ethers, and their derivatives will also be examined in this direction.

EXPERIMENTAL PART.

In the attempts to prepare stereoisomeric chlorimidoesters, we were guided by the idea that an acylchloramide which forms with alkalies rearranging salts, possibly of a *syn*-series, might give by methylation with diazomethane[2] an ether of the same reactive series, different from the chlorimidoether obtained in the usual way by the action of hypochlorous acid on an imidoether.[3] At the same time it was desirable to obtain any stereoisomers in a solid form, and for that reason derivatives of metanitrobenzoic acid were first employed. We found that the action of hypochlorous acid on methylimidometanitrobenzoate resulted in the formation of both stereoisomers at the same time. They were separated from each other by repeated recrystallization. The action of diazomethane on nitrobenzchloramide gave a much less pure product, from which only the higher-melting isomer, which we will call the α-body for the present, was obtained in a pure condition.

m-Nitrobenzchloramide, $m\text{-}NO_2C_6H_4CONHCl$, was prepared according to the method of Graebe and Rostovzeff[4] from nitrobenzamide and sodium hypochlorite. Acetic acid precipitated the chloramide as a colorless, gelatinous mass. When dry, it was recrystallized from a mixture of acetone and benzene. It melts at 183° to 184° with decomposition. A quantitative yield was obtained.

For analysis, as in the case of all the nitrogen halides described in this paper, the compound was dissolved in alcohol and treated with a solution of potassium iodide acidified with acetic acid. The iodine which was liberated was titrated against standard thiosulphate solution.

I. 0.1114 gram substance gave 0.0196 gram Cl.
II. 0.1699 gram substance gave 0.0302 gram Cl.

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[1] Stieglitz: This JOURNAL, *loc. cit.*

[2] Stieglitz and Ransom: *Ibid.*, **29**, 49 (1903).

[3] Stieglitz: *Ibid.*, 18, 751 (1896).

[4] Ber. d. chem. Ges., **35**, 2750 (1902).

	Calculated for $C_7H_5O_3N_2Cl$.	Found. I.	II.
Cl	17.67	17.55	17.77

Action of Diazomethane on m-Nitrobenzchloramide.

Methyl Chlorimido-m-nitrobenzoate (*α-body*), $NO_2C_6H_4C(:NCl)OCH_3$.—The chloramide is suspended in anhydrous ether and diazomethane passed into the mixture until the solution appears distinctly yellow. The action takes place tolerably fast at ordinary temperatures and may be hastened by warming the mixture on the water-bath. It is complete as soon as all the solid substance has dissolved. On evaporation of the ether in a vacuum, long, prismatic crystals of the chlorimidoether are deposited. It is purified by repeated precipitation from its solution in chloroform by means of low-boiling ligroin.

I. 0.1532 gram substance gave 0.0250 gram Cl.
II. 0.1365 gram substance gave 0.0222 gram Cl.

	Calculated for $C_8H_7O_3N_2Cl$.	Found. I.	II.
Cl	16.52	16.33	16.29

The compound crystallizes from chloroform and ligroin in fan-like groups of silky needles. By the slow evaporation of the solutions, long prisms or rectangular plates are obtained (see Fig. I.). The substance melts at 86°.5 to 87°.5 without decomposition, and melts at the same point if it is allowed to solidify and is heated once more. It is easily soluble in chloroform, benzene, and acetone; quite soluble in ether and warm ligroin, hardly soluble in cold ligroin. A more de-

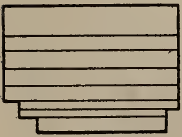

Fig. 1. *α*-body.

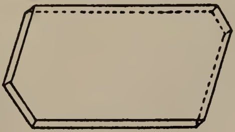

Fig. 2. *β*-body.

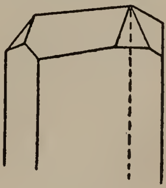

Fig. 3.

tailed description of the physical properties of the compound will be given below, when it will be compared with the stereoisomer, which will be called for the present the β-body.

The constitution of the α-body was determined by treatment of the substance with dry hydrogen chloride in the presence of ligroin. The hydrochloride of methyl imido-*m*-nitrobenzoate was obtained according to :[1]

$$NO_2C_6H_4C(:NCl)OCH_3 + 2HCl \rightarrow NO_2C_6H_4C(:NH)OCH_3,HCl + Cl_2.$$

The hydrochloride of the imidoether decomposed, when melted, into methyl chloride and *m*-nitrobenzamide :

$$NO_2C_6H_4C(NH)OCH_3,HCl \rightarrow CH_3Cl + NO_2C_6H_4CONH_2.$$

The amide was identified by its melting-point, which was not depressed by the admixture of some synthetic *m*-nitrobenzamide (m. p. 142°).

The hydrochloride of methyl imido-*m*-nitrobenzoate obtained from the α-body was also identified by the fact that with cold water it gave ammonium chloride and methyl *m*-nitrobenzoate (m. p. 75° to 76°) :

$$NO_2C_6H_4C(NH)OCH_3,HCl + H_2O \rightarrow NO_2C_6H_4CO_2CH_3 + NH_4Cl.$$

In a roughly quantitative study of the action of dry hydrogen chloride on the α-body, 0.163 gram substance gave 0.151 gram of the hydrochloride of the imidoether, or 91.8 per cent of the theoretical yield. From the salt, 0.109 gram methyl *m*-nitrobenzoate was obtained by the action of water, that is 86.5 per cent of the calculated yield. The fact thus established, that in the α-body the methyl group is attached to the oxygen atom of the acid radical, is confirmed by the proof brought below, that the only possible constitutional isomer, *m*-nitrobenzmethylchloramine, $NO_2C_6H_4CO(NClCH_3)$, is an entirely different substance.

The action of diazomethane on *m*-nitrobenzchloramine takes place, therefore, according to :

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[1] Stieglitz : This JOURNAL, 18, 751 (1896).

$$NO_2C_6H_4CONHCl + CH_2N_2 \rightarrow NO_2C_6H_4C(OCH_3)(:NCl) + N_2,$$

and the constitution of the α-body is that given in this equation.

The Action of Hypochlorous Acid on Methyl Imido-m-nitrobenzoate.

The hydrochloride of methyl imido-*m*-nitrobenzoate (15 grams) is added rapidly to a large excess of sodium hypochlorite[1] at 30°.[2] An oil separates instantly and then solidifies in a few moments. The crude product is washed with cold water and then dried on clay plates. The average yield is 9 to 10 grams. The crude product melts at 63° to 68°. After two recrystallizations from ligroin the α-modification of methyl chlorimido-*m*-nitrobenzoate is first precipitated, together with small quantities of the β-body, which lowers the melting-point from 87° to 79°. That the substance is otherwise pure is shown by the following analysis:

0.1891 gram substance gave 0.0315 gram Cl.

	Calculated for $C_8H_7O_3N_2Cl$.	Found.
Cl	16.52	16.64

From the mother-liquors, crystals are obtained which melt at 56° to 63°, and the analyses of which also prove them to be pure methyl chlorimido-*m*-nitrobenzoate, but these crystals consist of mixtures of the two stereoisomeric bodies (the α- and the β-modifications). The analyses of several of these low-melting mixtures are given in order to show that we have to do from the beginning with mixtures of the pure isomers:

I. 0.1660 gram substance gave 0.0273 gram Cl.
II. 0.2021 gram substance gave 0.0336 gram Cl.
III. 0.1468 gram substance gave 0.0244 gram Cl.

	Calculated for $C_8H_7O_3N_2Cl$.	Found.		
		I.	II.	III.
Cl	16.52	16.44	16.63	16.63

From this mixture the two isomers were isolated in a pure condition by repeated recrystallization. We found the best procedure to be the following: The crude product is extracted three times with some boiling ligroin (b. p. 40°) and the residue is dissolved in chloroform and an excess of ligroin added to the solution. The α-body is precipitated in a fairly pure condition (m. p. 79°). By repeated recrystallization from chloroform and ligroin, it is obtained absolutely free from the β-body, and melts then at 87°.5. This melting-point is the same as that of the compound obtained from nitrobenzchloramide and diazomethane. A mixture of crystals of the compound prepared by the two methods of formation also melted at 87°.5. The formation of methyl chlorimido-*m*-nitrobenzoate (α-body) from methyl imido-*m*-nitrobenzoate and hypochlorous acid is expressed by the equation:

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[1] Prepared according to Graebe's method (*loc. cit.*).

[2] At 0° the reaction-products and the yields are the same.

$$NO_2C_6H_4C(:NH)OCH_3 + HOCl \longrightarrow NO_2C_6H_4C(:NCl)OCH_3 + H_2O.$$

Methyl Chlorimido-m-nitrobenzoate (*β-body*), $NO_2C_6H_4C(:NCl)OCH_3$. — The second stereoisomer, the β-body, is obtained from the first extracts of the crude material with boiling ligroin and from the mother-liquors obtained in the isolation of the α-body. After the evaporation of the solvents, the residue which still contains considerable quantities of the α-body, is dissolved once more in chloroform, ligroin added to the solution, and, after a short time, the supernatant liquid poured off from the precipitated crystals of the α-body, and allowed to evaporate spontaneously. Needle-shaped crystals of the less soluble α-modification, mixed with some of the β-form, are deposited on the sides of the vessel, and larger, rhombic crystals of the β-body are deposited on the bottom of the vessel. The latter are now almost pure and melt at 79°. The addition of some of the α-body depresses the melting-point to 63° to 70°. One or two further recrystallizations by the method of evaporation, as just described, raise the melting-point of the β-modification to 81°–82°, and further recrystallizations then leave the melting-point unchanged. The yield of the pure β-body was rather small, no doubt partly in consequence of the very long method of purification that had to be used. Several grams, however, were obtained in the course of our working up some 100 grams of crude material in several portions.

I. 0.1133 gram substance gave 0.0189 gram Cl.
II. 0.1601 gram substance gave 0.0264 gram Cl.

	Calculated for $C_8H_7O_3N_2Cl$.	Found. I.	II.
Cl	16.52	16.68	16.50

The β-body has the same constitution as the α-body. The possibility of its having been formed by a molecular rearrangement[1] according to

$$NO_2C_6H_4C(OCH_3)(NCl) \rightarrow NO_2C_6H_4CO(NClCH_3),$$

was excluded by the preparation of *m*-nitrobenzoylmethylchloramine (see below) as well as by the action of dry hydrogen chloride on the β-body in the presence of ligroin. In the latter experiment, exactly the same result was obtained as in the case of the α-body. The hydrochloride of methyl imidonitrobenzoate was formed. It melted at 127° with evolution of methyl chloride and formation of *m*-nitrobenzamide. The latter was recrystallized once from hot water and melted at 140°. Mixed with some synthetically prepared *m*-nitrobenzamide (m. p. 142°), it melted at 141°. The hydrochloride of the imidoether also gave, with water, methyl *m*-nitrobenzoate (m. p. 77°). In a roughly quantitative experiment we obtained from 0.179 gram of the purest β-compound 0.160 gram of the hydrochloride of the imidoether, or 94 per cent of the calculated amount. From the salt, 0.118 gram of methyl *m*-nitrobenzoate (m. p. 76° to 77°) was obtained by the action of water, that is 88 per cent of the calculated amount. A mixture was prepared of the methyl *m*-nitrobenzoate (m. p. 76° to 77°) obtained from the β-body and the methyl *m*-nitrobenzoate (m. p. 76° to 77°) obtained from the α-body (see above). The mixture also melted at 76° to 77°. There is no doubt, therefore, that in both the α- and β-bodies the methyl group is attached to the oxygen atom of the acid radical, and the nitro group is in the same position (meta) relative to the acid radical—in a word, that the two bodies have the same constitution and are methyl chlorimido-*m*-nitrobenzoates.

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[1] Imidoethers suffer such a rearrangement when they are heated with methyl odide, but not under the conditions used above.

N-Methyl-m-nitrobenzchloramide, $NO_2C_6H_4CO(NClCH_3)$, was prepared in order to exclude the possibility that we had mistaken it for one of the described modifications of the isomeric oxygen ether of the chloramide. Two grams of *m*-nitrobenzmethylamide (m. p. 176°), prepared from *m*-nitrobenzoylchloride and methylamine, was suspended in 100 cc. of water at 40°, and the chlorine evolved by the action of 8 grams of potassium permanganate on hydrochloric acid was passed into the mixture. The crystals were converted into a more flocculent precipitate. The compound was washed with water and then dried and recrystallized once from ligroin (b. p. 70° to 80°).

0.2143 gram substance gave 0.0356 gram Cl.

	Calculated for $C_8H_7O_3N_2Cl$.	Found.
Cl	16.52	16.62

The melting-point of this nitrogen ether was found to be 76° to 77°, which is rather close to the melting-points of the isomeric oxygen ethers. But we found in repeated experiments that mixtures of equal quantities of the nitrogen ether (m. p. 77°), and either the α-body (m. p. 87°) or the β-body (m. p. 81°) invariably melted much lower than any of the compounds, *viz.*, at 60° to 68°. There can be no doubt, therefore, that the nitrogen ether is entirely distinct from either of the two other isomers. It crystallizes in thick, monoclinic prisms with characteristic ends (see Fig. III.), quite different from the crystal forms of the two oxygen ethers. Treated with dry hydrogen chloride in the presence of ligroin, it is converted into *m*-nitrobenzmethylamide, a reversal of the method we used in preparing it.

$$NO_2C_6H_4CONHCH_3 + Cl_2 \rightleftarrows NO_2C_6H_4CONClCH_3 + HCl.$$

Comparison of the α- and β-Modifications of Methyl Chlorimido-m-nitrobenzoate.

The Crystal Forms.—The difference in the crystalline structure of the two stereoisomers is apparent even to the naked eye. The α-body forms needles which have a soft, silky luster; the β-body crystallizes in granular masses. Under the microscope the α-compound appears in long needles, grouped in clusters. When it is allowed to crystallize slowly, by the evaporation of its solutions at ordinary temperatures, it forms rectangular plates (see Fig. I.). The β-compound appears under the microscope in the form of very thin rhombohedric plates, which grow in separate crystals (see Fig. II.).

The Molecular Weight.—The molecular weights were determined by the cryoscopic method, benzene being used as solvent. In the calculation of the results, 53 was used as the constant for benzene, this being its theoretical value as calculated from the melting-point and the heat of fusion of the solvent. If the empirical constant, 49, is taken, as is often done, the molecular weights found for the α- and β-varieties are about 8 per cent lower than those given below, but they still agree perfectly with each other and satisfactorily with the theoretical molecular weight.

1. The α-body (m. p. 86° to 88°). 21.79 grams solvent.

I. 0.1596 gram substance gave 0°.189 depression.[1]
II. 0.3098 gram substance gave 0°.360 depression.
III. 0.4624 gram substance gave 0°.518 depression.

	Calculated for $C_8H_7O_3N_2Cl$.	Found.		
		I.	II.	III.
Molec. wt.	214.5	204	206	215

2. The β-body (m. p. 77°).[2] 21.03 grams solvent.

I. 0.1444 gram substance gave 0°.184 depression.
II. 0.3054 gram substance gave 0°.375 depression.
III. 0.4788 gram substance gave 0°.569 depression.

	Calculated for $C_8H_7O_3N_2Cl$.	Found.		
		I.	II.	III.
Molec. wt.	214.5	196.5	202.5	207

3. A mixture of the α- and β-bodies (m. p. 67°).[3] 21.89 grams solvent.

I. 0.1468 gram substance gave 0°.168 depression.

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[1] The mean of two or three readings is always given.

[2] The melting-point fell to 63° to 65° when a little of the α-body was added to the substance.

[3] Analysis: Calculated, Cl 16.53; found, Cl 16.63.

II. 0.2988 gram substance gave 0°.331 depression.
III. 0.4572 gram substance gave 0°.500 depression.

	Calculated for $C_8H_7O_3N_2Cl$.	Found. I.	 II.	 III.
Molec. wt.	214.5	210	216	217

The Melting-points.—1. Each isomer, added to the other one, both being absolutely pure, causes a decided depression of the melting-point of the body used. The melting-point of the α-body is depressed from 87° to 63°–65°, that of the β-body from 82° to 63°–65°, when approximately equal quantities of the two isomers are mixed and the depression is roughly in proportion to the amount of the foreign isomer added.

2. Each body, when it is melted and allowed to solidify again, always gives the same melting-point as the original substance used.[1] There is, consequently, no transformation of one isomer into the other when the bodies crystallize from the liquid condition.

3. If the α-body is fused and made to solidify again with the aid of a glass rod, to which a very small quantity of the β-body has been made to adhere, it still remains the α-body in spite of the contact with the β-isomer at the moment of crystallization. In consequence of the admixture of the small quantity of the foreign isomer, its melting-point sinks from 87°.5 to 85°–86° and it is reduced to 63° to 70° by the addition of still more of the β-form.

Exactly the same results are obtained with the β-body when it is allowed to crystallize in contact with very small amounts of the α-body. It always preserves its own identity; the melting-point is never raised but is depressed, roughly, in proportion to the amount of the foreign isomer used. The same observations are also made when the liquid condition is produced by evaporation of a solution rather than by fusion and crystallization allowed to proceed in contact with the foreign isomer.

These results, together with the fact that a transformation of either of the isomers into the other one has never been observed under any conditions, and that the two isomers crystallize side by side from the same solutions in ligroin, completely exclude, we believe, the possibility that the two forms are physical (crystal) isomers of the same compound.

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[1] The compounds must be perfectly pure. Otherwise the β-form occasionally shows, after fusion and recrystallization, a depression of 10°, probably in consequence of some decomposition (coloration).

Physical and structural isomerism thus being excluded and the molecular weights of the two bodies being identical, the latter must be stereoisomers. They are, therefore, no doubt *syn*- and *anti*-isomers, as explained in the introduction (page 400). No other known form of stereoisomerism would obtain for compounds of this constitution. As no reliable basis for distinguishing either form as the *syn*- or *anti*-isomer has yet been found, we will leave the determination of this question to a future investigation.

The Action of Heat on the Stereoisomers.

The action of heat on the two stereoisomers was studied first as being of peculiar interest, because the corresponding sodium salt of *m*-nitrobenzbromamine,

$$NO_2C_6H_4C(:NBr)ONa,$$

suffers a "Beckmann rearrangement" when it is warmed in an aqueous[1] or alcoholic[2] solution. If the alkali metal is only necessary to produce the double bond between carbon and nitrogen in order to effect the rearrangement,[3] then at least one of the stereoisomeric esters should suffer a similar rearrangement when heated or even warmed.

1. 0.0778 gram of the almost pure β-compound (m. p. 77° to 79°) was heated for forty minutes at 80° to 85° in a flask closed by a tube containing calcium chloride. A trace of substance sublimed. The residue (0.0766 gram) was analyzed by means of potassium iodide and thiosulphate and gave 16.78 per cent active chlorine (16.53 per cent is the calculated amount for the unchanged substance). In a second experiment, some of the purest preparation of the β-compound (m. p. 81° to 82°) was heated for one hour to 80° to 85°.

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[1] Hoogewerff and van Dorp : Rec. trav. chim., Pays-Bas., 8, 193 (1888).

[2] Folin : This JOURNAL, **19**, 325 (1897).

[3] Hantzsch : Ber. d. chem. Ges., **35**, 3580 (1902).

After solidifying, it again melted at 81° to 82°, and the addition of some of the α-body depressed the melting-point 16°. Consequently, prolonged heating at 80° produces neither a "Beckmann rearrangement" of the β-body nor a transformation into the α-form.

2. 0.0686 gram of the purest β-body was heated for five minutes at 130° to 140°. The residue gave 16.78 per cent active chlorine (calculated 16.53 per cent). Heating the β-body even to 140°, therefore, does not produce a rearrangement. In two other experiments with the β-body, heating to 140° caused in the one case a slight depression of its melting-point (from 82° to 76°), in the second case no depression at all, and in both cases the admixture of some α-body caused a decided depression of the melting-point. Consequently, there is no transformation of the β-body into the α-compound even at 140°.

3. Analogous experiments were carried out with the α-body. Heating it a half hour at 90° to 95°, or five minutes at 130° to 140°, left the body unchanged. Mixed with purest α-body, the solidified, heated sample showed no change of melting-point, and mixed with some β-compound, its melting-point was decidedly depressed, as usual. The α-body, consequently, suffers neither a "Beckmann rearrangement" nor a transformation into the β-body when heated as high as 140°.

CHICAGO, April, 1903.

Contribution from the Kent Chemical Laboratory of the University of Chicago.

THE "BECKMANN REARRANGEMENT." IV.

BY JULIUS STIEGLITZ AND RICHARD B. EARLE.

PART I.

The Formation of Acylalkylureas in Hofmann's Reaction.

In the preparation of an alkylamine, according to Hofmann's method, from an acid halogenamide or from an acid amide, bromine and alkali, by a "Beckmann rearrangement" of the acidamide,[1] an acylalkylurea is often obtained[2] as a by-product, and it frequently is the main product if an excess of the acid amide is used. Thus 2 molecules of acetamide treated with 1 molecule of bromine and 2 of alkali give a very good yield of acetylmethylurea,[1] only 1 molecule of the amide suffering the characteristic rearrangement:

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[1] Hoogewerff and van Dorp: Rec. trav. chim. Pays-Bas., **6**, 373 (1887); **8**, 173 (1889), etc.; Stieglitz: This JOURNAL, **18**, 751 (1896); **29**, 49 (1903).

[2] Hofmann: Ber. d. chem. Ges., **15**, 412 (1882).

$$2CH_3CONH_2 + Br_2 + 2NaOH \rightarrow CH_3CONHCONHCH_3 + 2NaBr + 2H_2O \quad (1).$$

In the higher aliphatic series the urea is the main product,[2] even when no excess of the acid amide is used, if aqueous solutions of an alkali are employed to effect the rearrangement. The yield of amine is, consequently, a very poor one. In alcoholic solutions, specific precautions must be taken if a complete rearrangement of a higher aliphatic acid amide is desired, otherwise the acylalkylurea is again the chief product obtained.[3]

The ready formation of these alkylacylureas has been ascribed[4] to the supposed fact that the alkyl isocyanate[5] which forms the first tangible product of the rearrangement of the acylhalogenamide, combines with any excess of acid amide which may be present. The action is supposed to go according to the following two stages:

$$RCONHHal + KOH \rightarrow CO:NR + KHal + H_2O; \quad (2)$$

$$CO:NR + RCONH_2 \rightarrow RCONHCONHR. \quad (3)$$

But this latter condensation actually takes place readily only at elevated temperatures, and Dr. Elizabeth Jeffreys,[6] working under the direction of the one of us, was able to show that neither phenyl isocyanate nor chlorformanilide can be made to combine with an acid amide in the presence of alcohol, a urethane being invariably produced rather than an acylalkylurea.

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[1] Hofmann: Ber. d. chem. Ges., **14**, 2725 (1881).

[2] Turpin: *Ibid.*, **21**, 2488 (1888).

[3] Jeffreys: This Journal, **22**, 14 (1889). See also Swartz: *Ibid.*, **19**, 295 (1897); and Folin: *Ibid.*, **19**, 325 (1897).

[4] Hofmann: Ber. d. chem. Ges., **15**, 410 (1882); Graebe and Rostovzeff: *Ibid.*, **35**, 2747 (1902).

[5] Or the halogen formamide, (Hal)CONHR, derived from it, Graebe: *Loc. cit.*; Hoogewerff and van Dorp: *Loc. cit.*

[6] *Loc. cit.*, p. 42.

The present investigation was undertaken with the object of determining the real course of the formation of acylalkylureas in Hofmann's reaction, and especially of ascertaining whether their formation under the conditions described above could mean that isocyanates cannot always be accepted as the first intermediate products of the rearrangement of acid halogenamides.[1]

Having found, with Dr. J. H. Ransom, that acid chloramides are very readily methylated by the action of diazomethane,[2] the one of us suspected that the formation of acylalkylureas in Hofmann's reaction is due to the condensation of a molecule of an isocyanate—formed by the rearrangement of 1 molecule of an acid halogenamide—with a second molecule of the acid halogenamide itself, an acylhalogenalkylurea being formed according to:

$$\mathrm{RCONH(Hal) + KOH \longrightarrow RN:CO + KHal + H_2O;} \quad (4)$$

$$\mathrm{RCONH(Hal) + RN:CO \longrightarrow RCON(Hal)CONHR.} \quad (5)$$

The urea, containing a nitrogen halide group, would be readily saponified in an alkaline solution[3] and form a hypochlorite, or hypobromite, and an acylalkylurea:

$$\mathrm{RCON(Hal)CONHR + KOH \longrightarrow RCONHCONHR + KOHal.} \quad (6)$$

The hypochlorite or hypobromite would then be available to act on a further molecule of acid amide, if such were still present, and thus complete the reaction according to the proportions expressed summarily in equation (1).

We have found that, both in the aliphatic and in the aromatic series, acid chloramides do condense, in fact, very readily and sometimes almost explosively with isocyanates, according to equations (5) and (6). Acylalkylureas are obtained very easily at ordinary temperatures in the presence of alkalies, under conditions, therefore, such as actually exist when Hofmann's reaction is carried out. As determined once more, aliphatic and aromatic acid amides do not respond at all to

[1] Stieglitz: This JOURNAL, *loc. cit.*

[2] *Ibid.*, **29**, 49 (1903).

[3] Slosson: *Ibid.*, **29**, 289 (1903).

the action of isocyanates under these circumstances. The formation of acylalkylureas in Hofmann's reaction is consequently due to the ready condensation of an isocyanate, the primary product of the rearrangement of a molecule of an acid halogenamide, with a second molecule of the latter, and to a subsequent saponification of the condensation-product. The action is, therefore, now also in complete harmony with the conception that an isocyanate may always be considered to be the first product of the "Beckmann rearrangement" of an acid halogenamide.

If the condensation of an aromatic isocyanate with an acid halogenamide is carried out in the absence of alkali under conditions, therefore, which would not lead to the saponification of the acylhalogenalkylurea formed primarily—see equations (5) and (6)—the urea is frequently found to suffer spontaneously an inter- or intramolecular migration of the halogen atom into the aromatic nucleus:

$$\mathrm{RCON(Hal)CONHC_6H_5} \rightarrow \mathrm{RCONHCONHC_6H_4(Hal)}. \quad (7)$$

This rearrangement is somewhat analogous to the transformation of acylphenylhalogenamines into acylhalogenanilides,[1]

$$\mathrm{RCON(Hal)C_6H_5} \rightarrow \mathrm{RCONHC_6H_4(Hal)},$$

but it differs from the latter in the fact that the halogen is not attached to the same nitrogen atom as the phenyl group into which it migrates. As the question of the nature of this change of position was not involved directly in our main problem we have left it for possible future investigation. It presents three interesting possibilities: An intramolecular migration between groups of atoms more widely separated than in all the well-known analogous rearrangements; an intermolecular action in contrast to the intramolecular transformation of the acylphenylhalogenamines;[2] and the most attractive possibility of a sequence of two migrations of the chlorine atom as the radical of hypochlorous acid, first from the one nitrogen atom to the other more positive one—as acyl groups actually are known to migrate[1]—and then from the second nitrogen atom into the phenyl ring of the same aniline group.

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[1] Bender: Ber. d. chem. Ges., **19**, 2272 (1886); Stieglitz and Slosson: *Ibid.*, **28**, 3266 (1896); Slosson: *Loc. cit.*; Chattaway and Orton: J. Chem. Soc. (London), **77**, 134 (1900).

[2] Blanksma: Rec. trav. chim. Pays-Bas., **21**, 366 (1902).

EXPERIMENTAL PART.

The Action of p-Chlorphenyl Isocyanate on Benzchloramide.

To 4.6 grams (1 mol.) of benzchloramide[2] were added 3 grams (1 mol.) of *p*-chlorphenyl isocyanate,[3] and a solution of 0.9 gram of sodium hydroxide in 9 cc. water. The reaction disengaged considerable heat, and it was necessary to moderate it by cold water. The mixture was shaken vigorously at intervals for half an hour, then the red precipitate was brought on a filter and thoroughly washed with water, alcohol, and finally, ammonia. The substance was extracted several times with boiling alcohol to insure the removal of traces of impurities. The insoluble residue melted at 227°, and was identified as symmetrical benzoyl-*p*-chlorphenylurea by the determination of the melting-point of a mixture of the substance with some of the urea which was prepared synthetically and melted at 235° to 237°. The mixture melted at 233° to 235°. *p*-Chlorphenyl isocyanate had condensed, therefore, with benzchloramide under the conditions of Hofmann's reaction to form symmetrical benzoyl-*p*-chlorphenylurea according to equations (5) and (6).

Symmetrical Benzoyl-p-chlorphenylurea, $C_6H_5CONHCONHC_6H_4Cl$.—The urea was prepared synthetically in two ways: By the action of *p*-chlorphenyl isocyanate on benzamide at 150°, and by the action of benzoyl chloride on *p*-chlorphenylurea. The latter method gave the purest substance. A mixture of benzoyl chloride and the urea was heated for an hour at 110° to 130°. The product was extracted several times with hot alcohol and the very difficultly soluble residue recrystallized from a large amount of boiling alcohol. The compound melted then at 235° to 237° and an analysis, (I.), proved its purity. When equivalent quantities of *p*-chlorphenyl isocyanate and benzamide were heated to 150°, the mixture foamed and then quickly solidified. The product, washed for some time with hot alcohol, was analyzed without further purification (Analysis II.). It formed a mass of white needles and melted at 234° to 236°.

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[1] This JOURNAL, **23**, 1 (1900).

[2] Graebe and Rostovzeff: Ber. d. chem. Ges., **35**, 2750 (1902).

[3] The isocyanate was prepared from *p*-chlorphenylurethane and phosphorus pentachloride, according to Lengfeld and Stieglitz: This JOURNAL, **16**, 70 (1894); Folin: *Ibid.*, **19**, 336 (1897).

I. 0.3026 gram substance gave 0.1581 gram AgCl.
II. 0.2973 gram substance gave 0.1601 gram AgCl.

	Calculated for $C_{14}H_{11}O_2N_2Cl$.	Found. I.	Found. II.
Cl	12.92	12.92	13.31

The Action of Phenyl Isocyanate on Benzchloramide.

This reaction was studied first in the absence of water and alkali. Phenyl isocyanate[1] (1.2 grams) was dissolved in 5 cc. dry benzene and warmed with dry benzchloramide (2 grams). At 77° all the chloramide had dissolved and the liquid became filled with a crystalline solid. After fifteen minutes, it was brought on a filter, washed with cold alcohol and some ammonia, and then thoroughly with boiling alcohol. The insoluble residue melted at 225°, and when added to synthetic symmetrical benzoyl-*p*-chlorphenylurea, it did not appreciably depress the latter's melting-point. It consisted, therefore, of benzoyl-*p*-chlorphenylurea, and it was formed, evidently, as the result of a condensation of phenyl isocyanate with benzchloramide and a subsequent migration of the chlorine atom into the benzene nucleus (see equations 5 and 7).

The action of phenyl isocyanate on benzchloramide in the presence of alkali was next tried. Benzchloramide (1.6 grams) was dissolved at 0° in a 20 per cent solution (7.5 cc.) of sodium hydroxide and this solution added all at once to the phenyl isocyanate (1.1 grams), the mixture being vigorously shaken. A reaction ensued instantly, the odor of hypochlorous acid (from the hydrolysis of some of the hypochlorite formed in the reaction) was developed, and a reddish precipitate formed. The latter was washed with alcohol and ammonia, and recrystallized from hot alcohol. It then melted at 205°, and when it was mixed with some synthetically prepared symmetrical benzoylphenylurea (m. p. 205°) its melting-point remained unchanged. The condensation had, consequently, taken place as expected, according to the equations (5) and (6). It may be added that the reaction does not take place smoothly unless there is at least one equivalent of alkali present as required by these equations.

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[1] The phenyl isocyanate was prepared from phenylurethane and phosphorus pentachloride, according to the method of Lengfeld and Stieglitz: *Loc. cit.* See Dains: J. Am. Chem. Soc., **21**, 165 (1899).

Phenyl isocyanate also condenses readily with benzbromamide under these same conditions, symmetrical benzoylphenylurea being again formed as the product of the action.

Phenyl Isocyanate and Benzamide.

Benzamide is much less reactive towards phenyl isocyanate than are its chlorine and bromine derivatives, and it does not condense at all with the isocyanate under the conditions of Hofmann's reaction. On warming a solution of the two substances as high as 100°, we found that no reaction had ensued and the benzamide was recovered unchanged. When benzamide was shaken with phenyl isocyanate (1 mol.) and an equivalent amount of sodium hydroxide, in aqueous solution, at ordinary temperatures until no odor of phenyl isocyanate remained discernible, the main reaction-product was aniline, and the benzamide was recovered unchanged. The aniline, obviously, was produced by the action of the alkali on the isocyanate.

The Action of Phenyl Isocyanate on Acetchloramide.

Symmetrical Acetylphenylurea, $CH_3CONHCONHC_6H_5$.—To one equivalent of sodium hydroxide (a 10 per cent solution) 1 molecule of acetchloramide was added and the solution poured at once on an equivalent weight of phenyl isocyanate. The solid, which quickly separated, was collected on a filter, washed with some alcohol and ammonia, and recrystallized from hot water. It melted at 183° to 184°, and a mixture of it and some pure symmetrical acetylphenylurea (m. p. 183° to 184°) gave the same melting-point. The action had proceeded, therefore, as expected, according to

$$CH_3CONHCl + C_6H_5NCO + NaOH \rightarrow CH_3CONHCONHC_6H_5 + NaOCl.$$

Acetamide is not acted upon by phenyl isocyanate, when the two are brought together in the presence of an equivalent amount of a five per cent solution of sodium hydroxide. The acetamide may be recovered, together with carbanilide and aniline, decomposition-products of the isocyanate.

The Action of Methyl Isocyanate on Acetchloramide.

Symmetrical Acetylmethylurea, $CH_3CONHCONHCH_3$. — Acetchloramide (1.8 grams) was dissolved in 5.5 cc. of a 20 per cent solution of caustic potash at 0°, and the solution added rapidly to 1.1 grams methyl isocyanate. A violent reaction occurred instantly and completed itself in less than a minute. A white solid filled the liquid. A little ammonia was added to the mixture, the solid collected on a filter, and washed with some cold water. It was fully identified in the usual way as symmetrical acetylmethylurea, by its melting-point (178°.5), and by the fact that this melting-point was not depressed by the addition of some synthetic acetylmethylurea to the reaction-product.

Methyl isocyanate does not combine with acetamide under the same conditions under which it reacts so vigorously with acetchloramide. Not a trace of acetylmethylurea could be obtained, the isocyanate being decomposed into methylamine and carbonic acid.

PART II.

Diacylchloramines.

When benzoylphenylchloramine is decomposed by heat, a little benzoyl chloride is formed,[1] possibly according to the following reaction :[2]

$$C_6H_5CONClC_6H_5 \rightarrow C_6H_5COCl + C_6H_5N:. \qquad (1)$$

It was hoped that diacylchloramines might decompose more readily in an analogous fashion, *viz.*, according to

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[1] Chattaway and Orton : J. Chem. Soc. (London), **79**, 462 (1901) ; Slosson : This JOURNAL, **29**, 305 (1903).

[2] The nature of the nitrogenous decomposition-product has never been determined. See Stieglitz : This JOURNAL, **29**, 49 (1903).

$$(C_6H_5CO)_2NCl \rightarrow C_6H_5COCl + C_6H_5CON:. \qquad (2)$$

An acylimide, with a univalent nitrogen atom, might thus result, which would be identical with the hypothetical substance that is supposed by the one of us to be an important intermediate product in the "Beckmann rearrangement" of acylchloramides, acylazides, oximes, etc.[1] A study of dibenzoylchloramine was, therefore, undertaken in order to ascertain whether it would suffer a "Beckmann rearrangement" under the influence of heat. The experiments showed that the decomposition takes a different course, benzonitrile, chlorine, and benzoyl chloride being the main products. This would indicate that a breaking down into benzonitrile and benzoyl hypochlorite[2] is the primary change:

$$(C_6H_5CO)_2NCl \rightarrow C_6H_5CN + C_6H_5COCl.$$

This decomposition is entirely analogous to that which the parent substance, dibenzamide, undergoes when it is heated :[3]

$$(C_6H_5CO)_2NH \rightarrow C_6H_5CN + C_6H_5COOH.$$

In order to determine whether a small part of the dibenzoylchloramine had suffered a "Beckmann rearrangement," the decomposition-products were completely saponified and tested for aniline, but only doubtful traces of the latter could be detected. This showed that none of the substance had undergone the rearrangement. When dibenzoylchloramine was heated with freshly ignited calcium oxide, the result was the same.

Dibenzoylchlorimide, $(C_6H_5CO)_2NCl$.—The diacylchlorimides were found so sensitive to water, which hydrolyzes them to hypochlorous acid and diacylimides, that it was found necessary to exclude water entirely in order to prepare dibenzoylchlorimide in a pure condition. Two grams of the silver salt of dibenzoylimide, dried at 100°, were suspended in 15 cc. anhydrous chloroform and 0.44 gram carefully dried chlorine passed into the mixture. After filtration the chloroform was evaporated *in vacuo* in a desiccator and the residue recrystallized from ligroin (b. p. 70° to 80°).

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[1] Stieglitz : This JOURNAL, *loc. cit.*, and **18**, 751 (1896).

[2] See Schützenberger's chlorine acetate : Ann. Chem. (Liebig), **120**, 113 (1861).

[3] Krafft : Ber. d. chem. Ges., **23**, 2391 (1890).

I. 0.1379 gram substance gave 0.0184 gram active Cl.

II. 0.1547 gram substance gave 0.0206 gram active Cl.

	Calculated for $C_{14}H_{10}O_2NCl$.	Found. I.	II.
Cl	13.65	13.37	13.32

Dibenzoylchlorimide crystallizes in white needles, which melt at 86°.

Three grams of the chlorimide were heated in a distilling-flask connected with a condenser, in a metal-bath. Decomposition set in at 240° to 260°, and proceeded smoothly, the substance turning dark red. The temperature was kept at 250° to 260° for five minutes. Ammonia was added to the cooled contents of the flask. Benzonitrile, benzoic acid, and benzamide were the only products that could be identified, besides some chlorine which escaped during the decomposition of the substance. In a second experiment, the reaction-product was saponified by being boiled with sulphuric acid (sp. gr. 1.44), and the mixture tested for aniline as follows: It was made alkaline, distilled with steam, and the distillate tested directly for traces of aniline, as well as extracted with ether, the test for aniline being made after the evaporation of the extract in the cold. No trace of aniline could be found. Preliminary tests showed that a few milligrams of carbanilide or phenylurea, subjected to this treatment, easily give the aniline reactions.

An intimate mixture of 1.5 grams dibenzoylchloramine and 0.2 gram freshly ignited calcium oxide was heated to 170° to 180°. Benzonitrile and its polymer, cyanphenine, were the only nitrogenous products obtained in quantity. Tests for aniline were made as in the previous experiment. Once a trace of it was shown by the chloride of lime test, but in a duplicate experiment not even this trace was found.

It is evident, therefore, that dibenzoylchlorimide does not show any tendency to suffer a "Beckmann rearrangement."

CHICAGO, April, 1903.

ON THE OCCURRENCE OF INVERTASE IN PLANTS.

BY J. H. KASTLE AND MARY E. CLARK.

Quite recently the attempt has been made in this laboratory to obtain inulase free from other ferments. During our search for a convenient source of this enzyme we have been impressed with the wide distribution of invertase in the vegetable kingdom.

An examination of the literature of the subject revealed that Kosmann[1] had found invertase in the buds and leaves of young trees. In 1886 van Tiegham[2] found this ferment in pollen grains, and later Reynolds Green[3] confirmed these observations and made the further observation that the ferment rapidly increases during germination, particularly if the pollen be germinated on solutions of cane-sugar. Béchamp[4] found it in the petals of flowers, and also in the juice of the mulberry, but failed to find it in the foliage leaves of the plants which he examined. Gonnermann[5] found it in the leaves of the sugar-beet; Atkinson and Kellner[6] in rice; Mieran[7] in the ripe fruit of the banana; and Martinand[8] in crushed grapes, that had been sterilized previous to crushing. Brown and Morris[9] in their interesting contribution to the chemistry and physiology of foliage leaves also record the fact that the air-dried leaves of a species of *Tropæolum* can invert cane-sugar. They did not seem to regard their experiment, however, as absolute proof that the leaf tissue contained invertase, since the inversion of the sugar according to them might have been accomplished by a small amount of fungi growing on and in the leaf. At the same time they point out the desirability of further work in this direction. The latest observations bearing upon this point that have come under our notice are those of O'Sullivan.[1] This observer found invertase in the roots, stems, and leaves of the maize, oats, and wheat, and proved that in the case of these plants at least the occurrence of the ferment could in no way be attributed to the presence of micro-organisms.

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[1] Bull. Soc. Chim., **27**, 251 (1877).

[2] Bull. Soc. Bot. de France, **33**, 216 (1886).

[3] Phil. Trans., **185**, B. 385 (1894).

[4] Compt. rend., **59**, 496 (1864).

[5] Bied. Centr., **28**, 550 (1899).

[6] Ztschr. physiol. Chem., **14**, 297 (1890).

[7] Chem. Ztg., **14**, 1283.

[8] J. Chem. Soc. (London). Abs., **80**, II., 35 (1901).

[9] J. Chem. Soc. (London), Trans., 1893, p. 636.

While, therefore, a good deal had already been done in studying the occurrence and distribution of this enzyme in plants, it seemed that much yet remained to be accomplished, particularly in the way of studying the distribution of the ferment in the several organs and tissues of the plant. Indeed, the results thus far obtained in the present investigation are sufficient to indicate the far-reaching importance of invertase in plant metabolism.

Mode of Procedure and Results.

In searching for the ferment in various tissues, the following mode of procedure has been followed as far as practicable. The portion of the plant under investigation was cut up into fine pieces and thoroughly dried in the air at 40° C. It was then reduced to a fine powder in a porcelain mortar, sometimes alone and sometimes with the addition of a weighed amount of white sand. One-tenth gram portions of the finely powdered tissue were then weighed out and put into small glass bottles, of 70 cc. capacity. To one bottle there was then added 50 cc. of water and 0.5 cc. of toluene, the latter being employed as antiseptic. This served as an active control experiment and enabled us to get an idea of the amount of reducing sugars originally present in the tissue under investigation, or that formed from its own reserve materials during the progress of the experiment. To a second bottle containing 0.1 gram of the tissue there were added 50 cc. of water, 0.5 gram cane-sugar, and 0.5 cc. of toluene, and to a third, 50 cc. of a 1 per cent starch paste and 0.5 cc. of toluene. With certain of the tissues investigated control experiments were also tried, in which 0.1 gram of the tissue was boiled with water and then made up to 50 cc. with the required amount of cane-sugar or starch. In no case, however, did these control experiments show any increase in the amount of reducing sugars over the quantity present in the active controls, and hence nothing further need be said concerning them. In order to determine whether the ferment was present in the fresh tissue, or formed therein as the result of drying, certain experiments were tried with the freshly macerated tissue. In these experiments somewhat larger quantities of the tissue were employed in order to compensate for the large amounts of water which the fresh tissue contained. The actual amounts employed in such experiments are indicated in the following table. It also occasionally happened that smaller quantities than 0.1 gram of the tissue were employed. This is also indicated in the table.

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[1] J. Chem. Soc. (London), Trans., 1960, pp. 691–696.

After standing in the incubator at 38° to 40° C., for the desired interval, usually twenty-four hours, the bottles were removed and 10 cc. of the contents of each boiled with 2 cc. of standard Fehling solution. A comparison of the several experiments of the given series with the active control experiment of that series, as to the amount of reduction, indicated, at least approximately, the inversive and diastatic activity of the particular plant tissue under investigation. Up to this time no attempt has been made to determine accurately the amount of cane-sugar which could be inverted by a given amount of plant tissue. The object has been simply to demonstrate the presence or absence of the ferment.

Up to the present, nineteen different species of plants, representing fourteen different families, have been examined for the ferment. The results are given in the annexed table, together with such experimental data as are required for an understanding of the results.

An examination of the results given in the above table shows that invertase is a ferment of wide, if not universal, occurrence in the vegetable world. It has been found abundantly in every plant thus far examined, and these have been selected in such a way that out of the nineteen different species examined, fourteen different families of plants are represented. It will be seen further that in the several organs of plants invertase is more constant in its occurrence than

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No. of experiment.	Name of plant	Part of plant tested	Quantity of plant-tissue used. Gram.	Result of test with Fehling solution			Remarks
				Active control	Cane-sugar.	Starch	
1	White radish, *Raphanus sativus*	Leaves	0.1	Trace of reduction	Good reduction	Good reduction	
2	" " " "	" fresh	0.5	" " "	Complete reduction	Complete reduction	
3	" " " "	Root	0.05	Slight reduction	Nearly complete reduction	" "	
4	" " " "	" fresh	0.5	Distinct "	Good reduction	" "	Starch completely liquefied
5	Red radish	Leaves	0.1	No reduction	Complete reduction	Nearly complete reduction	
6	Carrot, *Daucus Carota*	"	0.1	" "	" "	Trace of reduction	
7	" " "	Root	0.1	Good "	Better reduction than in control	Better reduction than in control	" "
8	Jerusalem artichoke, *Helianthus tuberosus*	Leaves	0.1	No "	Good reduction	No reduction	
9	" " " "	Tubers, young	0.1	Distinct reduction	Complete reduction	Same as control	
10	" " " "	" " fresh	0.5	Slight "	" "	Not tried on starch	
11	" " " "	" old, dry	0.05	" "	Good reduction	Slightly more than control	
12	Potato, *Solanum tuberosum*	Leaves	0.1	" "	Complete reduction	Good reduction	
13	" " "	Tubers, very young, just forming	0.03	No reduction	Good reduction	No reduction	
14	" " "	" young	0.05	" "	" "	" "	
15	" " "	Old tuber, sprouted, part near sprout	0.05	" "	Some "	" "	
16	" " "	Sprout	0.01	" "	Complete reduction	Slight reduction	
17	" " "	" fresh	0.5	Good reduction	" "	Good "	Tested after standing 4 hours at 40° C.
18	Experiment 17 continued	" "	0.5	" "	" "	Larger reduction than control	Time, 21 hours
19	" " "	Tuber, very small, just forming	0.01	No reduction	Good reduction	No reduction	" 7 days at 40° C.
20	" " "	" young, ¾ inch in diameter	0.05	" "	" "	" "	" 7 " " " "
21	*Dahlia variabilis*	Leaves	0.1	" "	Complete reduction	Complete reduction	
22	" "	Bulbs	0.1	Trace of reduction	Slight "	Slight "	
23	Dandelion, *Taraxacum officinale*	Leaves	0.1	No reduction	Complete "	" "	
24	" " "	Roots	0.1	" "	Good reduction	" "	
25	Onion, *Allium cepa*	Bulb, old	0.1	Trace of reduction	Trace of reduction	Trace of reduction	
26	" " "	" "	0.1	" " "	No reduction	No reduction	
27	" " "	Sprouts, from old bulb	0.1	Good reduction	Complete reduction	Nearly complete reduction	
28	*Spirogyra*,	Entire plant	0.035	No "	Some reduction	No reduction	
29	" Experiment 28 continued		0.035	" "	Good "	Slight reduction	
30	*Sorghum vulgare saccharatum*	Young plant, entire	0.1	Slight "	Complete reduction	Complete reduction	
31	Sugar-beet, *Beta vulgaris*	Leaves	0.1	No "	" "	" "	
32	" " " "	Root	0.1	Distinct reduction	Good reduction	Some reduction	
33	Maize, *Zea Mays*	Seedling, stem and leaves	0.1	" "	Complete reduction	Complete reduction	
34	" " "	" roots	0.1	" "	" "	" "	
35	" " "	Large plant, leaves	0.1	Trace of "	Nearly complete reduction	" "	
36	" " "	" " roots	0.1	Distinct "	Complete reduction	" "	
37	" " "	" " stalk	0.1	Good "	" "	" "	
38	" var. sugar corn	" " leaves	0.1	Distinct "	Good reduction	Nearly complete reduction	
39	" " " "	" " roots	0.1	" "	Slightly more than control	Good reduction	
40	" " " "	" " stalk	0.1	Good "	Good reduction	" "	
41	" " " "	Grain, unripe	0.05	Distinct "	Nearly complete reduction	Nearly complete reduction	Starch liquefied
42	" " " "	" "	0.05	" "	Complete reduction	Complete reduction	" "
43	Annual Wormwood, *Artemisia annua*	Leaves	0.1	Trace of "	" "	" "	" rapidly liquefied
44	Pine, species not determined	"	0.1	Slight "	" "	Slightly more than control	
45	Grape, cultivated, Ives Seedling	Fruit, unripe	0.1	" "	" "	" " " "	
46	Hemp, *Cannabis sativa*	Root	0.1	" "	Good reduction	Somewhat more than control	" liquefied
47	" " "	" of plant infected with broom rape	0.1	No reduction	Complete reduction	Good reduction	" "
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49	Soy-bean, *Glycine hispida*	Leaves	0.1	" "	" "	Complete reduction	All starch liquefied
50	" " " "	Tips of growing stem	0.1	Slight reduction	" "	" "	
51	" " " "	Pod, with forming seeds	0.1	" "	" "	" "	
52	" " " "	Root	0.1	No reduction	Good reduction	" "	
53	Broom-rape, *Orobanche ramosa*	Entire plant	0.05	Very slight red'ct'n	Complete reduction	Slight reduction	
54	" " " "	Seed pod	0.05	No reduction	" "	" "	
55	" " " "	Entire plant, very young, fresh tissue	0.5	Good "	" "	More reduction than control	
56	" " " "	Enlarged bulbous portion at base of full-grown plant	0.5	Trace of reduction	" "	Scarcely more than control	
57	" " " "	Roots, fresh	0.25	No reduction	" "	No reduction	
58	" " " "	Seeds, yellow, fresh	0.03	" "	" "	Not tested on starch	
59	" " " "	" " dried in air	0.03	" "	" "	" " " "	
60	" " " "	" " " at 40° C in air	0.04	" "	" "	Slight reduction	
61	" " " "	" brown, ripe, air-dried	0.03	" "	Good reduction	Not tested on starch	
62	Sweet potato, *Ipomœa Batatas*	Leaves, young, near tip of vine	0.1	Slight reduction	Complete reduction	Nearly complete reduction	
63	" " " "	" mature	0.1	No reduction	" "	Complete reduction	
64	" " " "	Tubers, young, fresh	0.5	Slight reduction	Good reduction	" "	
65	Locust, *Robinia Pseudacacia*	Stem	0.1	No reduction	Some "	Good reduction	Starch partly liquefied
66	" " "	Root	0.1	Slight reduction	More reduction than control	Complete reduction	" completely liquefied
67	" " "	Leaves, young, near tip of branch	0.1	Trace of reduction	Complete reduction	" "	
68	" " "	Leaves, mature	0.1	" " "	Nearly complete reduction	Some reduction, more than control	

diastase. Contrary to the views and results of Bêchamp, invertase occurs abundantly in the leaves of plants, and his failure to find it in the leaves of the locust, *Robinia Pseudacacia*, is probably to be ascribed to the fact that he attempted to prepare clear aqueous extracts of the ferment, whereas, except under great pressures, this is impossible in many cases. The same difficulty was experienced by Wortmann[1] in attempting to extract diastase from foliage leaves, and yet it has been conclusively proven by Brown and Morris[2] that the leaves of most, if not all, of the starch-forming plants contain this enzyme.

In the second place, it will be observed that invertase occurs in the plant in some rather unexpected associations. It has been found, for example, in the growing tubers of the potato and the artichoke, and also in the sprouts of the potato. Now, as inulin is the chief reserve material of the artichoke and starch that of the potato, one would naturally be inclined to expect the occurrence of relatively large amounts of inulase and diastase, respectively, in these young tubers, and also that of diastase in the sprout of the potato, and while these ferments are present in these organs of these plants, they are not present in such quantities as invertase, or at any rate cane-sugar is much more easily hydrolyzed by these tissues, under antiseptic conditions, than inulin or starch.

Thirdly, it will be observed that invertase is not confined to those plants which store up cane-sugar as the characteristic reserve material. On the contrary, while it has been found in such of these as have thus far been examined, *viz.*, the sorghum plant and sugar-beet, it has also been found abundantly in those plants which store up starch and inulin as reserve materials, and what is of still greater interest, it has been found in those very organs of the plant that are actively engaged in storing up starch and inulin, for example, in the growing tubers of the potato and artichoke and in the unripe grain of the maize. It is our intention to investigate more fully the occurrence of invertase in the reserve organs of these plants in the hope of learn-ing something further as to the part played by this ferment in the storing up of starch and inulin.

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[1] Bot. Ztg., 1890, p. 583.

[2] J. Chem. Soc. (London), Trans., 1903, pp. 604-677.

The fact that invertase and cane-sugar are both of such general occurrence in plants is sufficient in itself to indicate the extreme inportance both of this carbohydrate and this ferment in plant metabolism. Curiously, two exactly opposing views have been held regarding the origin and fate of cane-sugar in the plant. As the result of his studies on the occurrence and products of alteration of cane-sugar in plants, Kayser[1] reached the conclusion that this carbohydrate results from starch by the direct action of a diastatic ferment, and that it is then transformed into invert sugar by the action of a ferment similar to invertin, before it is consumed in the respiratory processes in the plant. On the other hand Brown and Morris,[2] ten years later, arrived at the conclusion that the starch formed by the chloroplasts is not, strictly speaking, autochthonous, but that it owes its origin to cane-sugar. According to these observers, cane-sugar is antecedent to starch and is probably the first product of photo-synthesis. According to them it serves as a temporary reserve material and is probably to be regarded as the starting-point in all of the metabolic changes taking place in the leaf.

The fact that invertase occurs so generally in foliage leaves and that it is so widely disseminated throughout the several organs of the plant, lends additional support to the views advanced by Brown and Morris, and the fact that it is also largely present in the reserve organs of the plants storing inulin as well as those storing starch, would seem to point to cane-sugar as the substance immediately antecedent not only to starch but to other reserve materials as well. It is known that, generally, any particular stereo-configuration on the part of a compound is preserved in its derivatives. Such being the case, and since, further, the molecule of cane-sugar is made up of a dextro- and a laevo-portion, it is readily conceivable that such optically active reserve substances as starch and inulin are produced from it, first by its conversion into invert sugar through the action of invertase and the subsequent polymerization of dextrose and levulose. The further fact that the simpler sugars resulting from the hydrolysis of cane-sugar belong to the aldose and ketose types, respectively, would seem to lend additional probability to the view that all of the more complex carbohydrates are derived originally from cane-sugar. The production of cane-sugar by the plant as the first temporary reserve material becomes readily intelligible on the supposition that *d*-glucose, *l*-glucose, *d*-levulose, and *l*-levulose are the first products of photo-synthesis, and that two of these, *viz.*, *l*-glucose and *l*-levulose are at once consumed to supply the immediate needs of the plant. *d*-Glucose and *d*-levulose might then go on accumulating in the cell until a certain concentration was reached when, under the influence of invertase, they would combine to form cane-sugar. This latter compound, then, would sustain to the plant the relation of a temporary reserve material to meet its more remote requirements or to be transformed into still more complex, less readily hydrolyzable reserve materials, such as starch and inulin, as the case might be. We are aware that the idea that the racemic forms of optically active compounds are always the first products of plant synthesis, is not shared by all chemists. It is worthy of note, however, that racemic compounds, as well as their active components, do occur in plants, and that certain of the fungi and micro-organisms display a selective action in the appropriation of optically active compounds as foods, thereby enabling us oftentimes to obtain optically active compounds from the racemic form.

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[1] Versuchsstationen, **29**, 460–473 (1883).

[2] J. Chem. Soc. (London), Trans., 1893, p. 673.

With the view of throwing further light on these interesting questions we hope, if the necessary materials can be secured, to make a thorough study of the conduct of the racemic forms of glucose and levulose towards the hydrolyzing enzymes and certain fungi and higher parasitic plants.

STATE COLLEGE OF KENTUCKY,
LEXINGTON, August, 1903.

ON A NEW METHOD FOR THE PREPARATION OF PURE IODINE.

BY LAUNCELOT W. ANDREWS.

The impurities to be looked for in iodine are moisture, hydriodic acid, bromine, chlorine, and cyanogen iodide. A number of processes have been suggested for obtaining a product free from these contaminations, among which may be mentioned the methods of Stas,[1] Wittstein,[2] Mohr,[3] Meineke,[4] and of Lean and Whatmough.[5] All these methods are either very elaborate, demanding no inconsiderable sacrifice of time, or, like the simple resublimation of iodine with potassium iodide, are inefficient. The reaction between fused potassium pyrochromate and potassium iodide, which occurs in accordance with the equation

$$5K_2Cr_2O_7 + 6KI = 8K_2CrO_4 + Cr_2O_3 + 6I,$$

seemed to offer a possible and simple method for obtaining pure iodine directly from the impure iodide. A preliminary experiment showed that by fusing a mixture of 29.5 grams of potassium pyrochromate with 20 grams of potassium iodide, practically the whole of the iodine was obtained in the free state. No iodine was set free on fusing a mixture of normal potassium chromate and iodide. A mixture of potassium bromide (6 mols.) with pyrochromate (5 mols.) furnished, on fusion, a trace of free bromine, but when to the same mixture a little normal potassium chromate had been added, no bromine was set free. It should be said that all mixtures were made by rubbing the constituents thoroughly together in a mortar.

These experiments made it appear almost certain that if potassium iodide and pyrochromate were mixed together, with the former in moderate excess of the amount required by the equation, a product free from bromine and chlorine would be assured. Accordingly, 28 grams of potassium pyrochromate were powdered with 20 grams of potassium iodide and 1 gram of potassium bromide and the mixture was fused in a wide, glass tube. Three and eight-tenths grams of the sublimate were tested in the following manner for bromine: The iodine was thrown into 100 cc. of hot concentrated ammonia and a slight excess[1] of silver carbonate was added and the solution filtered. From the filtrate the silver was precipitated by hydrogen sulphide and the liquid boiled down to a very small bulk with a little pure barium carbonate. The residue gave no reaction for bromine, either by the fluoresceïn test or on spectroscopic examination according to Lecoq de Boisbaudran.[2]

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[1] Nouvelles Recherches sur les Lois des Proportions Chimiques, p. 136.

[2] Dingler's Poly. Jour., **200**, 310 (1871).

[3] Titrir-Methode, 1874, p. 269.

[4] Chem. Ztg., **16**, 1219 (1892).

[5] J. Chem. Soc. (London), **73**, 148 (1898).

To summarize, the following are the necessary steps in the preparation of pure iodine by the method given; Pulverize potassium iodide with one and four-tenths times its weight of potassium pyrochromate, each salt having been, previously, separately fused to insure perfect dryness. Introduce the thoroughly incorporated mixture into a wide tube, closed at one end, and heat to about 200° in a current of dry air to expel any moisture which may have been taken up during the pulverization. Place a plug of dry glass wool over the mixture and wipe out carefully the interior of the tube above the plug with absorbent cotton secured to a glass rod. Slip over the open end of the tube a second, short one, fitting it as snugly as possible. Fix the tube at an angle with the horizontal and heat the powder gradually with a small flame, using, if necessary, a screen of asbestos board. Having sublimed the iodine into the upper part of the tube, cut off the latter, when cold, at a point 2 or 3 cm. above the glass-wool plug, or, if smaller amounts are being operated on, the tube can be melted off at the place indicated.

CHEMICAL LABORATORY,
STATE UNIV. OF IOWA,
July 6, 1903.

Since sending the foregoing communication to the editor of the AMERICAN CHEMICAL JOURNAL, it has come to my knowledge through the last number of the *Central-blatt* (**1**, 1435 (1903)) that L. L. de Koninck has published in the *Bulletin de l'Académie royale Belgique*, **17**, 15, a nearly identical method for the preparation of pure iodine. The priority, accordingly, belongs to him, but in view of the importance of the subject, it still appears worth while to publish the entirely independent confirmation of his results which my experiments afford; the more so since, so far as it is possible to judge from the abstract, his work does not directly demonstrate that the process can be so conducted as to insure the preparation of a product free from bromine.

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[1] Ascertained by acidifying a filtered sample with hydrochloric acid.

[2] Compt. rend., 91, 902 (1881). This method rests on the observation of barium bromide lines at wave lengths, 535.8 and 520.6

CHEMICAL LABORATORY,
STATE UNIV. OF IOWA,
July 25, 1903.

Contributions from the Sheffield Laboratory of Yale University.

CXIII.—ON IODOCYANIDES OF POTASSIUM AND CAESIUM.

BY C. H. MATHEWSON AND H. L. WELLS.

By dissolving iodine in concentrated solutions of potassium cyanide, Langlois[1] prepared a compound to which he gave a formula corresponding to $KI.4CNI.4H_2O$. Since this salt does not correspond to the alkali-metal trihalides or pentahalides, examples of which are $KCl.ICl$ and $KCl.ICl_3$, we have undertaken a new examination of Langlois' compound, and, having found that his formula was correct, except in regard to the amount of water in it, we have attempted to prepare caesium iodocyanides, which, in view of the great stability of the caesium perhalides, promised to be more stable than the rather unsatisfactory potassium compound. As the result of the latter investigation, we have obtained the single compound $CsI.2ICN$, which does not correspond to the potassium salt, but which may, perhaps, be regarded as showing analogy to the pentahalides, although no crystallographic resemblance to any of the latter could be made out by Professor Penfield, who kindly examined the crystals.

Potassium Iodocyanide, $KI.4CNI.H_2O$.—This compound was prepared by dissolving varying proportions of iodine in concentrated potassium cyanide solutions and also by adding large amounts of potassium iodide, together with iodine, to such solutions. No evidence of the existence of any other combination of potassium iodide and cyanogen iodide was found. The compound forms small, colorless needles, as described by Langlois. The substance is very unstable, giving off cyanogen iodide when exposed to the air, so that it was necessary to press it rapidly on paper for analysis. The following analyses were made of different products:

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[1] Ann. chim. phys. [3], 60, 220 (1860).

	Calculated for $KI.4CNI.H_2O$.	Found. I.	II.	III.
K	4.91	5.64	5.65	5.54
I	79.76	79.62	79.44	79.20
CN	13.06	12.48	12.24	12.59
H_2O (diff.)	2.26	2.26	2.67	2.67

It appears certain that Langlois obtained too much water in the compound, probably from insufficient drying. In fact, it seems quite possible that the substance is anhydrous, since our products could not be air-dried, and since the amount of water corresponding to 1 molecule is small.

Potassium was determined by carefully heating the compound and weighing the potassium iodide. Cyanogen was determined volumetrically with silver nitrate, after decolorizing the aqueous solution of the substance with sulphurous acid, and then making the liquid ammoniacal. After a permanent precipitate of silver iodide had appeared, indicating the end of the titration for cyanogen,[1] an excess of silver nitrate was added, the resulting precipitate was collected on a filter, extracted with ammonia, and the residual silver iodide was weighed in order to determine iodine.

Caesium Iodocyanide, $CsI.2ICN$.—This compound forms cinnamon-colored, orthorhombic plates, which are rather sparingly soluble in water. It is much more stable than the potassium compound, but still it gives off an odor of cyanogen iodide. It was prepared by dissolving iodine in caesium cyanide solution, but more conveniently, on account of the difficulty of preparing caesium cyanide, by dissolving caesium iodide and cyanogen iodide in warm water and cooling.

[1] Denigès: Ann. chim. phys. [7], 6, 381.

Caesium triiodide was almost invariably deposited after the iodocyanide had formed, but there was no difficulty in getting out the crystals of the latter in a satisfactory condition. Seven crops were prepared under the following conditions :

	I.	II.	III.	IV.	V.	VI.	VII.
CsI, grams	10	10	10	5	2.5	1	1
CNI, "	1	2	5	5	5	5	10

In each case the solution in water was about 25 cc. in volume. These gave the following analyses :

	Calculated for CsI.2CNI.	Found. I.	II.	III.	IV.	V.	VI.	VII.
Cs	23.50	23.57	....	....	28.59	....	....	23.41
CN	9.18	9.03	9.12	9.20	9.31	9.30	9.18	9.24
I	67.31	67.65	....	67.88	....	68.15	....	67.53

It is evident from these results that only a single compound is formed under widely varying conditions.

The methods used for the analysis of this salt were similar to those used for the potassium compound.

New Haven, Conn., June, 1903.

Contributions from the Sheffield Laboratory of Yale University.

CXIV.—ON A COMPOUND OF MERCURIC CYANIDE AND CAESIUM IODIDE.

By C. H. Mathewson and H. L. Wells.

It has been found by one of us[1] that mercuric iodide and caesium iodide form a series of five double salts, and that the two chlorides form the same number of compounds, while mercuric iodide and caesium chloride give only a single double salt, $Cs_2HgCl_2I_2$. The present investigation has been undertaken in order to find out how mercuric cyanide and caesium iodide would behave in the formation of double salts, and the results show that these salts combine in only one proportion, forming the compound $CsI.Hg(CN)_2$.

It is to be noticed that this double salt belongs to a different type from that of the chloriodide, but the point appears to be established that the presence of two different acid radicals prevents the formation of a variety of compounds. It is well known that mercuric cyanide combines with many other salts, and hence it shows a remarkable tendency toward double-salt formation, but in spite of this tendency, and in spite of the facility with which caesium salts form double compounds, only a single double salt is formed in this case.

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[1] Am. J. Sci., 44, 221 (1892).

The salt under consideration was prepared by cooling solutions containing caesium iodide and mercuric cyanide in proportions by weight varying from 1 : 15 to 10 : 1. When more than 15 parts of mercuric cyanide to 1 of caesium cyanide were used, either indefinite mixtures or crops of nearly pure mercuric cyanide were obtained. The double salt forms thin, white, pearly plates, which can scarcely be distinguished in appearance from pure mercuric cyanide. The salt is readily recrystallized from water, and thereby remains unchanged in composition. Acids decompose the salt with evolution of hydrocyanic acid and formation of mercuric iodide.

The following analyses were made of different crops :

	Calculated for $CsI.Hg(CN)_2$.	Found.					
		I.	II.	III.	IV.	V.	VI.
Cs	25.97	25.40	25.81	25.58	25.87	25.66	25.40
Hg	39.06	39.67	39.17	39.13	39.09	....	....
I	24.80	24.48	24.69	24.70	24.63	....	....
CN	10.15	....	....	....	9.80	....	....

NEW HAVEN, CONN., July, 1903.

REVIEWS.

BRIEFWECHSEL ZWISCHEN J. BERZELIUS UND F. WÖHLER, IM AUFTRAGE DER KÖNIGL. GESELLSCHAFT DER WISSENSCHAFTEN ZU GÖTTINGEN. Mit einen Commentar von J. VON BRAUN. Herausgegeben von O. WALLACH. Erster Band mit Berzelius' Bildniss. pp. xxii + 718. Zweiter Band mit Wöhler's Bildniss. pp. 744. Leipzig : Verlag von Wilhelm Engelmann. 1901.

This important work should have been reviewed long ago. It ought to be read by every chemist. It reveals to us the characters of the two great men as nothing else could at this time. The letters cannot be abstracted. They must be read from beginning to end. This requires time, but the time will be well spent.

Some years ago, in view of the occurrence of the hundredth anniversary of Wöhler's birth, July 31, 1900, the Royal Society of Sciences in Göttingen planned to publish this correspondence if Wöhler's letters to Berzelius could be secured.

These were left to the Swedish Academy of Sciences. Fortunately, the Academy gave its consent to the publication. Wöhler had carefully preserved the letters of Berzelius, and had placed them in charge of the Swedish Academy, on condition that they should not be published before January 1st, 1900.

The correspondence began in 1823, when Wöhler asked to be admitted into Berzelius' laboratory, and ended in 1848 with the death of Berzelius. This is an extremely important period in the history of chemistry. Professor Wallach, the editor, says: "It is intended by this publication to facilitate the study of one of the most interesting chapters of chemical research and to lead the younger chemists to trace to their sources the important investigations from which our present chemistry has sprung. Nothing could be more profitable for the healthy development of our science than for the young chemists, who are just coming to the front, to accustom themselves to look backward out of the turbulence of the present and to get thoroughly under the influence of the thoughtful and almost painfully thorough investigations which stamped the time of Berzelius and Wöhler as the classic age of chemistry."

As is well known, after Wöhler's return to Germany from Sweden, he soon began the translation of the great Lehrbuch of Berzelius and also of Berzelius' Jahresbericht. This work he kept up until the death of Berzelius. The Lehrbuch filled ten large volumes and five editions were issued, though the fifth was not finished. This literary work alone was the work of a giant. Few men have done as much. But the most important work of both Berzelius and of Wöhler was that of teaching and investigating. Both of them contributed enormously to the advancement of chemistry. How they could have done the amount of work they did without breaking down it is, at first sight, difficult to see. And yet, after reading this correspondence, the explanation appears. *They kept at it.* They rarely forgot their work. Occasionally they grew weary and talked of giving it up, but they did not give way to their impulses, and to the end they kept in harness. Even after it became impossible for Berzelius to write, he dictated letters about the Lehrbuch, the Jahresbericht, and his relations to Liebig.

Every chemist who thinks he is overworked ought to study the life of Berzelius. To be sure, probably but few could stand the strain that he subjected himself to, but there is a large margin between the day's work of the average chemist and the day's work of Berzelius or of Wöhler.

Much of the correspondence has to deal with details touching the Lehrbuch and the Jahresbericht. Typographical errors, nomenclature, arrangement, cuts, etc., are the chief topics of many of the letters, but, as the editor remarks in the preface, any attempt to condense these letters would have taken away from the clearness of our view into the scrupulous care with which Berzelius dealt with such matters.

In order to make the references of the writers to chemical topics clear, Dr. J. von Braun has appended notes that will be of great aid in enabling younger chemists to understand the significance of many passages in the letters that would otherwise be more or less obscure. These are clearly written and show a thorough grasp of the subject.

The writer of this notice has marked throughout the two volumes many especially striking paragraphs. It would be interesting here to quote these with or without comment, but on looking through the book he finds that they would fill many pages and only a few can be given. Vol. II., page 79, Wöhler writes: "Dann habe ich Dir meinen Dank zu sagen für Deinen Brief von 28 Dec. und das damit gekommene Thierchemie-Manuscript. Das gibt wieder ein gutes Stück Arbeit. Bei der wenigen Zeit, die mir dazu übrig bleibt, würde ich den Muth verlieren hätte ich nicht Dich als Muster des unbegreiflichsten Fleisses vor Augen, sähe ich nicht, welch ganz andere und viel grössere Arbeit Du mit der Ausarbeitung des Originals hast, als ich mit der Uebersetzung habe. Doch ich fürchte, diese Jeremiaden über Zeitmangel habe ich schon mehr als einmal vorgebracht. Verzeihe dass ich wiederholt Dich damit schwäche. Inzwischen entspringen sie auch aus dem betrübten Gefühl, dass ich für das was mir am Meisten am Herzen liegt für meine eigenen Arbeiten so gut wie keine Zeit übrig behalte, dass ich die Minuten dazu stehlen muss, dass in einer so zerstückten und zerstreuten Zeit keine Untersuchungen zu Stande kommen können. Diese Klagen sollen also zugleich vor Dir als Entschuldigungen gelten, dass ich nicht so productiv bin, als Du von mir erwartest."

Vol. II., p. 134, Berzelius writes: "Es muss in wissenschaftlicher Hinsicht ein Etwas geben ähnlich dem, was man in socialer Takt nennt, ein Gefühl das, ohne dass man für den Augenblick sich die Gründe dafür klar macht einem sagt, was zu thun sich nicht schickt oder was angeht, und welches Gefühl einige in hohem Grade besitzen und andere, wenn sie auch mit noch mehr Genie als diese begabt sind, ganz und gar entbehren. Wenn ich eine unrichtige theoretische Darstellung sehe, so fühle ich es, auch wenn die richtige mir unbekannt ist, ohne es mir noch klar machen zu können, dass sie falsch ist, so wie das Ohr einen falschen Ton hört. Und wenn eine richtige Darstellung kommt, so wird sie sofort erkannt, sie erfreut und macht einen angenehmen Eindruck, so wie eine reine Intonation. Etwas ähnliches muss auch in der Wissenschaft mit im Spiele sein, denn wir sind in vielen Dingen wie Maschinen, und was ein jeder von uns in richtiger Spekulation vermag oder nicht vermag, beruht ganz und gar auf der verschiedenen Organization unserer Gehirne. Der Versuch, demjenigen einen Begriff von schöner Musik zu geben, der den Unterschied zwischen falschen und reinen Tönen nicht hört, ist ebenso vergeblich wie denjenigen, der nicht angeborenen Takt besitzt, in Opinionsachen zu überzeugen. Er kann, falls er nicht voreingenommen ist, das richtige als Gedächtnisaufgabe lernen, aber er ist immer bereit, es gegen anderes auszutauschen, denn er empfindet nicht, dass dieses weniger richtig ist.—Oder—ist dieses nur eine dumme Idee von mir?"

It appears from a passage in a letter written by Wöhler, April 25th, 1840 (Vol. II., p. 169), that the well-known satire on the substitution theory that was published in the Annalen (Bd. **33**, 308) was written by Wöhler. Liebig published it without consulting the writer. Wöhler says in regard to this: "Dass Dir der Einfall über die Substitutions-theorie nicht missfallen hat und dass Du bemerkst, er verdiene allgemeiner gelesen zu werden, ist mir eine wahre Beruhigung gewesen, da Liebig ihn, ohne mein Wissen und Willen, aber versteht sich ohne meinen Nahmen, wirklich drucken lassen, indem er ihn in dem einen und anderen Punkt etwas abgeändert und einige neue Witze hinzugefügt hat. Ehe ich nämlich den Brief, worin ich Dir den Spass geschrieben hatte, zumachte, kam ich auf den Einfall, denselben auch, weil er mir selbst gefiel, Liebig mitzutheilen und für ihn in Form eines aus Paris datirten Briefes abzuschreiben, ohne dass ich aber im Entferntesten daran dachte, dass er so toll sein würde ihn in den Annalen abdrucken zu lassen. Er ist mit S. Ch. Windler (Schwindler) unterzeichnet."

On page 267, Vol. II., occurs this advice to Wöhler: "Lieber Wöhler, arbeite tüchtig so lange Du noch Kräfte hast, denn Du glaubst nicht, was der Mensch für ein Vieh wird, wenn er zu altern anfängt." Berzelius was then in his 62nd year.

In 1841 (Vol. II., p. 274) Wöhler writes in regard to the work of translation to which he gave so much time: "Für

Niemand Anderes in der Welt als für Dich würde ich dieses Geschäft noch einmal übernehmen. Es ist nur Gefühl des Dankes und der Pflicht, nur Pietät gegen Dich, die mich dazu bestimmt."

Berzelius' relations to Liebig are illuminated by these letters. They respected each other and at times were positively affectionate, but at times they were quite the opposite. In 1842, Berzelius really thought Liebig was becoming insane, and writes (Vol. II., p. 298): "Liebster Wöhler! Ich schreibe Dir dieses in grosser Traurigkeit. Ich erhielt mit der letzten Post das Märzheft der Annalen, das ich am Sonntag auf dem Lande, wo ich nichts anderes zu thun hatte, durchlas und woraus ich nun deutlich ersehe, dass meine im letzten Briefe geäusserte Befürchtung, dass Liebig nahe daran sei, den Verstand zu verlieren, früher, als ich dachte, zur Wirklichkeit geworden ist und dass er nun das, was wir auf Schwedisch "galen" nennen, wirklich ist. Was soll man mit dem armen Manne thun? Wenn seine Freunde sich jetzt nicht um ihn bemühen, so kann er leicht unrettbar verloren gehen."

Wöhler defends Liebig warmly, while acknowledging that there appears to be some justification for the statements. He says, Vol. II., p. 301: "Es ist ein durchaus rechtlicher, ehrenhafter und nobeler Charakter, aber leidenschaftlich, unbesonnen und rücksichtslos. Ich missbillige im höchsten Grade diese Rücksichtslosigkeit, diese unwürdige Art der Polemik, diese anmaasliche Sprache in wissenschaftlichen Gegenständen; aber ich liebe ihn als einen meiner besten Freunde und verehre ihn als einen ausgezeichneten Geist."

Side lights are thrown upon the scientific partnership between Liebig and Wöhler. Berzelius has advised Wöhler to withdraw. To this Wöhler replies (Vol. II., p. 324): "Da ich von Liebig rede, will ich hier gleich die Bemerkungen in Deinem Brief von 9ten Aug., das gemeinschaftliche Arbeiten mit ihm betreffend, beantworten. Ich muss Dir im Allgemeinen beistimmen und anerkennen dass ich mit meinem Theil Ehre, unverdienterweise, etwas zu kurz komme. Aber was liegt daran, wenn die Sache an sich dadurch gewinnt, und dass ist ganz gewiss der Fall. Wir beiden, Liebig und ich, haben ungleiche Arten von Talent, die, zusammenwirkend, einander ergänzen und etwas zu leisten vermögen. Niemand erkennt diess mehr an als Liebig selbst, und Niemand lässt mir für den Antheil an unseren gemeinschaftlichen Arbeiten mehr Gerechtigkeit widerfahren als er, wenigstens privatim. Uebrigens wenn ich auf die öffentliche Meinung einen Werth

legen will, so wäre es, sollte ich denken, unklug gehandelt, gerade jetzt mich von ihm zurückzuziehen und aufzuhören, Arbeiten gemeinschaftlich mit ihm auszuführen. Doch ist diess nicht der Grund, warum ich ihm die Narcotin-Untersuchung zum Gegenstand einer gemeinschaftlichen Arbeit angeboten habe (was schon vor Empfang Deines Briefes von 9ten Aug. geschehen war). Es geschah diess, um ihm einen thätlichen Beweis meiner unveränderten Freundschafts-Gesinnungen gegen ihn zu geben, zu einer Zeit, wo von allen Seiten (zum Theil verdiente) Verdriesslichkeiten auf ihn losstürmten und er in diesem Zustande von Gereiztheit Gründe und Symptome zu sehen glaubte, dass auch ich ihn verleugnen und verlassen wollte."

The publication of the results of work done by a student under the direction of his teacher is touched upon in a letter from Wöhler (Vol. II., p. 395): "Da nun in neuerer Zeit häufig der Fall vorkommt dass nicht unwichtige Arbeiten von Eleven auf Veranlassung und unter Leitung ihrer Lehrer vorgenommen und dann die Resultate in den Lehrbüchern erwähnt werden, so kann oft die Frage enstehen, wessen Nahmen dabei als Autorität zu nennen ist. Dabei immer die Explication zu geben, dass es unter der Leitung von dem und dem geschehen sei, ist zu umständlich und passt nicht wohl für ein Lehrbuch. Für diese Fälle scheint mir daher der Ausweg, den Du einmal angewendet hast, im Allgemeinen der beste zu sein, nämlich die Arbeit als eine gemeinschaftliche des Lehrers und der Eleven anzuführen. So wäre also die obige Arbeit über die Wirkung des Chlors auf das Kohlensulfid als 'von Wöhler und Kolbe' zu bezeichnen. Ich hoffe, dass Du mir diese Bemerkung nicht als eine kleinliche Eitelkeit auslegen wirst."

To this Berzelius remarks (Vol. II., p. 401): "Es muss dort Wöhler und Kolbe richtig eingetragen werden; was Deinen Vorschlag betrifft in allen ähnlichen Fällen auf dieselbe Weise zu verfahren, so ist das wohl im Grunde das Richtige, aber was soll ein armer Kompilator machen, wenn er seinen Honig aus einem Journal holt, wo nur der Schüler als Verfasser angegeben ist. Das richtigste ist, ihn dadurch zu autorisieren, dass die Namen des Lehrers und des Schülers bei dem Artikel im Journal zusammenstehen. Einen solchen "blancbec" in seinem eigenen Namen ausfliegen zu lassen, verwöhnt so sehr, dass er stolz und eitel und anspruchsvoll wird. Dein Völckel z.B., wenn man das, was er unter der Leitung von Deiner Hand und von Deinem Kopfe hinsichtlich der Schwefelcyanverbindungen gemacht hat, mit dem vergleicht, was er

jetzt nachher auf eigene Faust und nach seinem eigenen Kopfe gemacht hat, welch ein Unterschied! und doch welche Ansprüche in der Art der Darstellung, er behandelt Liebig wie eine Prise Schnupftabak. Ich rate Dir desshalb nunmehr damit anzufangen, Deinen Namen neben den des Schülers auf solche Arbeiten zu setzen, zu denen Du in dem Laboratorium, dem Du vorstehst, die Anleitung giebst. Es bleibt immer eine Wahrheit das die Sache Dir gehört und die Arbeit dem Schüler."

But these few extracts must suffice. It is hoped that every earnest young chemist will carefully read the whole of the correspondence. He cannot fail to be interested and benefitted. Older chemists need no advice. I. R.

THE TEACHING OF CHEMISTRY AND PHYSICS IN THE SECONDARY SCHOOL. By ALEXANDER SMITH, B.SC., PH.D., Associate Professor in the University of Chicago, and EDWIN H. HALL, PH.D., Professor in Harvard University. New York, London, and Bombay: Longmans, Green & Co., 1902. pp. xiii + 377.

It would be well if every teacher of chemistry and of physics should not only read, but carefully study, this book. It is full of good common sense presented in an attractive way. It does not attempt to tell the teacher exactly what to do under all circumstances, but it does offer a great many valuable suggestions in a kindly and practical way. Neither author assumes the "high and mighty" attitude towards his readers. They show that they have lived and suffered, but that they have kept their eyes open and have learned something about teaching.

The first part, that which deals with chemistry, consists of eight chapters. These bear the headings: I. Introduction; II. Chemistry in the Curriculum; III. The Introduction of the Subject; IV. Instruction in the Laboratory; V. Instruction in the Classroom; VI. Some Constituents of the Course; VII. The Laboratory, Equipment, and Illustrative Material; VIII. The Teacher, His Preparation and Development.

The second part (pages 233 to 371) contains thirteen chapters with the following titles: I. Whether to be a Teacher of Physics; II. Preparation for Teaching; III. The Teacher as Student, Observer, and Writer; IV. Problems of Laboratory Practice; V. School Text-books of Physics; VI. Discovery, Verification, or Inquiry?; VII. The Technique of Laboratory Management; VIII. Lectures and Recitations; IX. Physics in Primary and Grammar Schools; X. Physics in Various Kinds of Secondary Schools; XI. On the Presentation of Dynamics; XII. Plan and Equipment of a Laboratory; XIII. Physics Teaching in Other Countries.

In his preface, Professor Smith says: "The book assumes the reader's familiarity with the science. Many brief references to chemical matters would have been greatly expanded or carefully limited if they had been intended for beginners. There has been no intention to recommend particular text-books. Many have been cited as possessing some point of special excellence, but this must not be taken to indicate emphatic approval of those works as wholes, say for use with a class of beginners."

In respect to advice about books, the authors have both been so extremely tolerant that the teacher will get the impression that any one of a dozen or more text-books will answer about as well as any other, though he will also get the impression, perhaps a proper one, that no matter what book he may choose he will probably wish that he had chosen another.

Professor Smith restates a fundamental truth that is never to be lost sight of when he says: "In all instruction the personality of the teacher is held to be a factor of not less importance than the nature of the subject taught. The close personal contact which laboratory instruction secures between the pupil and teacher, and the consequent greater opportunity which his personality has to impress itself upon the pupils is not one of the least of the benefits we are discussing."

Further, he says (p. 122): "One of the most serious faults of much chemistry teaching is that the pupils are allowed to work by themselves in the laboratory in the absence of the teacher." * * * "The disastrous blunder of permitting or encouraging unsupervised work seems to be commoner in colleges than in secondary schools. But, until it is recognized and remedied, we can never secure either culture or a knowledge of chemistry * * * ."

In regard to the time for the introduction of the atomic theory he says (p. 161): "It may be possible to introduce the atomic theory at an early stage without causing confusion and to talk to beginners of atoms when combining weights are intended, without obscurity, but I do not know any text-book in which this has been done successfully, and I could name many in which it has been attempted with disastrous results."

The passages above quoted will meet with the hearty approval of a good many teachers of chemistry—among them the writer of this notice.

Finally, let me quote a part of what the author has to say on the subject of the importance of a knowledge of physical chemistry for the teacher of chemistry: "On the whole, perhaps, after this discussion of some of the bearings of physical chemistry upon elementary chemistry, it may be a question whether, in the average course, time will be found for anything more than a touch of the subject here and there. The conclusion is inevitable, however, that the teacher himself must be thoroughly familiar with the results of physical chemistry and its applications to ordinary chemical phenomena, if the instruction he gives is to be thoroughly sound."

In the first part of the book, three misprints of proper names have been noted. On page 202, "F. W. Clark" should be "F. W. Clarke;" on page 221, "Ramay" should be "Ramsay;" on page 223, "Ritcher" should be "Richter."

Professor Hall's part of the book covers, to some extent, the same ground that Professor Smith's does, though the editor of the Series ("American Teachers Series"), Dr. James E. Russell, says: "The authors of the separate parts on chemistry and physics have conferred frequently during the progress of the work and have endeavored to avoid unnecessary duplication."

Professor Hall has had much to do with the working out of the Harvard *Descriptive List of Elementary Exercises in Physics*, and he naturally draws upon his experience in the use of this course, and those teachers who are following it should read what he has to say. The author says (page 315): "Physics is, at the best, hard for most minds, young or older; and if the teacher is blessed with the gift, or can by pains acquire the power, of presenting his subject in an attractive way, of making his teaching artistic in form as well as sound in substance, he will win not only the respect of his pupils but, what is perhaps to both sides more stimulating, their admiration." I. R.

TESTS AND REAGENTS, CHEMICAL AND MICROSCOPICAL. By ALFRED I. COHN, PH.G. New York: John Wiley & Sons. 1903. 8vo. pp. 383. Cloth, $3.00.

Chemists, and no doubt pharmacists and microscopists as well, are continually seeing in the literature references to tests and reagents that are known by their authors' names. It usually happens that the less common of them are not mentioned in the books at hand. The present work has been written with just this difficulty in view. The tests are arranged alphabetically, according to the names of the authors, and on the 338 pages devoted to them there are, on the average, 8 to the page. By far the greater number of these are of less importance to the chemist than to the other workers for whom the book is intended. The following examples will give an idea of the character of the book: Lythgoe (aniline orange in milk); Magini (stain for nervous centers); Lux (fatty oils in mineral oils); Lawrence (glycerine jelly); Johnson (sugar in urine); Eboli (alkaloids); Edlefsen (naphthalene); Drechsler (alcohol); etc. In the index the substances tested for are given with the names of the authors following. Here and there errors in spelling occur. We note, for example, "Hoffmann." On the whole, the book seems to be a valuable one, and should be in demand.

C. E. W.

QUANTITATIVE CLASSIFICATION OF IGNEOUS ROCKS, Based on Chemical and Mineral Characters, with a Systematic Nomenclature by WHITMAN CROSS, JOSEPH P. IDDINGS, LOUIS V. PIRSSON, HENRY S. WASHINGTON. University of Chicago Press. pp. 286.

The publication of this work by four of the leading petrographers of America marks a distinct epoch in the study of igneous rocks and the handling of chemical analyses in petrographical investigations. The principles of classification involved call for the careful determination of the chemical constituents of each rock, and a computation of these into certain well-defined mineral molecules which are to be known as standard minerals. It is proposed to base the new classification on the predominant mineral constituents thus derived, which fall into two broad classes; the *salic* minerals, rich in silica and alumina, such as the feldspars, quartz, leucite, and nepheline, and the *femic* minerals, rich in iron and magnesium, such as diopside, hypersthene, olivine, etc. According to the proportions of these salic and femic minerals, igneous rocks are divided into five Classes. Each Class in turn is divided, according to the relative proportion of the minerals belonging to the predominant group, into five Orders, which are in turn divided into five Rangs, according to the ratio of $Na_2O + K_2O : CaO$ or $CaO + MgO + FeO : Na_2O$. The Rangs are in turn subdivided into five or three Subrangs according to the ratio of $K_2O : Na_2O$ and $MgO : FeO$. Each of the several divisions is indicated by a characteristic termination in the nomenclature.

The use of this classification will cause all rock masses of the same chemical composition to fall together in a purely artificial classification regardless of the minerals formed during the consolidation of the rock magma. The authors believe that a natural classification of rocks is not obtainable with our present knowledge, and suggest the new classification with the hope that it will avoid the present multiplication of names and poorly defined rock types based upon mineralogical composition.

The adoption of this classification by the more advanced petrographers in America will necessitate greater accuracy in the analysis of the different chemical constituents, especially ferric and ferrous iron and the alkalies, as well as of the numerous constituents which are found in small quantities in igneous rocks, as shown by Hillebrand's excellent analyses.

E. B. M.

BENZOLTABELLEN. Darstellungsmethoden und Eigenschaften der einfacheren, technisch wichtigen Benzolderivate aus der Literature zusammengestellt von DR. CARL SCHWALBE, Privatdocenten an der Technischen Hochschule zu Darmstadt. Berlin: Gebrüder Borntraeger. 1903.

In this book of less than 270 quarto pages is contained a very large amount of information of value to every chemist who is interested in the derivatives of benzene and its homologues. The principal classes of compounds are taken up in order, beginning with the sulphonic acids, halogen derivatives, nitro derivatives, monamines, etc., and ending with the aldehydes, aldehydesulphonic acids, and the carbonic acids. Opening the book at random we come to 5-Sulphosalicylic acid. Under this heading are given six methods of formation of the acid, with references to the original literature in a parallel column. The properties are stated, again with literature references, and there are four articles cited in connection with the salts of the acid. Every one of the 250 or more compounds mentioned in the book is treated in a similar way. The book, apart from its large size, is not suited to the use of students in the laboratory on account of the brevity of the directions, but it will prove of great value to any one who wishes to learn the best methods of preparing benzene derivatives. It should find a place in every chemical library. C. E. W.

JAHRESBERICHT ÜBER DIE FORTSCHRITTE DER CHEMIE UND VERWANDTER THEILE ANDERER WISSENSCHAFTEN. Begründet von J. LIEBIG und H. KOPP. Unter Mitwirkung namhafter Fachgenossen herausgegeben von G. BODLÄNDER, W. KERP, und G. MINUNNI. Neuntes Heft. 1894. Braunschweig: Friedrich Vieweg und Sohn. 1902.

The "Jahresbericht" is so well known that its appearance calls for no comment except to note the fact that a new number has been issued. C. E. W.

LOIS GÉNÉRALES DE L'ACTION DES DIASTASES. Par VICTOR HENRI, Docteur en Philosophie (University de Göttingue), Docteur ès Sciences Préparateur de Physiologie a la Sorbonne. Paris: Librarie Scientifique A. Hermann. 1903. pp. 129.

The object of the author is to present the best work that has been done on the kinetics of enzyme action, and to consider the results obtained in the light of what is known of the kinetics of more simple chemical reactions. In the introduction he very briefly summarizes the present knowledge of catalysis of which, as he says, enzyme action is but a special case.

Only three enzymes are considered in this work, namely, invertase, emulsin, and diastase. Chapter I. contains a review of what has been done on the kinetics of the above-mentioned enzymes, especially the work of O'Sullivan and Thompson, Tammann, Duclaux, A. Brown, H. Brown and Glendinning, and Herzog. The remaining 75 pages of the monograph deal with the work of the author, and his theoretical conclusions, which are of much interest and importance and may be summarized as follows :

Invertase.—(1) The inversion of saccharose by this enzyme is more rapid than would be indicated by the logarithmic equation which applies to the inversion by acids. (2) Invert sugar inhibits the action of invertase, and this inhibition is due almost entirely to the fructose. The inhibitory action of invert sugar is greatest when only a small amount of saccharose is present and decreases as the amount of saccharose is increased. (3) For solutions of saccharose more dilute than N/10, the velocity of the inversion increases with the concentration of the saccharose. Between N/10 and N/2 the velocity is independent of the concentration, while above N/2 increase in the concentration of the saccharose decreases the velocity of the inversion. (4) The velocity of the inversion is proportional to the quantity of enzyme acting. (5) The author assumes that the enzyme forms intermediate combinations with the substance upon which it acts, and also with the substances produced by its action. In support of this view he points out that Emil Fischer found invertase to act only on those substances which on hydrolysis yield fructose, and connects this with the fact that he has found that the inhibitory action of invert sugar is due almost entirely to fructose. He further points out that whereas the velocity of inversion is largely independent of the saccharose present at the beginning of the reaction, yet the addition of saccharose during the course of the reaction increases the velocity of the inversion. He explains the inhibitory effect of the products of enzyme action as Tammann did, *viz.*, by the formation of combinations between the enzyme and these products. He does not consider the question of reversibility as an explanation of inhibition by the products of hydrolysis. (6) He believes that a state of equilibrium exists between the free enzyme and that combined with the substance upon which it acts and the products of the hydrolysis, and from this deduces the formula

$$\frac{dx}{dt} = \frac{k(a-x)}{1 + m(a-x) + nx},$$

where k is a constant proportional to the quantity of enzyme acting, m and n are constants which depend upon the composition of the medium and the temperature, and vary with different enzymes. They give k the same value whatever be the concentration of the saccharose and invert sugar. This equation was found to hold for the action of invertase on saccharose and also for emulsin acting on salicin.

Emulsin.—He studied its action on salicin and found the hydrolysis to be slower than would be indicated by the logarithmic equation. Otherwise the results were similar to those given above for the action of invertase on saccharose.

Diastase.—(1) The velocity of the formation of maltose from starch by diastase follows a curve parallel to that of the acid hydrolysis. (2) The quantity of starch present influences in a different manner the action of pancreatic diastase and that obtained from malt. (3) It is impossible to treat this reaction mathematically since so little is known of the intermediate steps in the hydrolysis. (4) If we assume m and n to be equal in the above-mentioned equation, the formation of maltose seems to follow the same law as was found to hold for invertase and emulsin. A. S. L.

THE PRINCIPLES OF ANIMAL NUTRITION. With Special Reference to the Nutrition of Farm Animals. By HENRY PRENTISS ARMSBY, PH.D., Director of the Pennsylvania State College Agricultural Experiment Station; Expert in Animal Nutrition, United States Department of Agriculture, First edition; first thousand. New York: John Wiley & Sons; London: Chapman & Hall, Limited. 1903. pp. 614.

As the author states in his preface, this book is not a treatise upon stock-feeding, but "an attempt to present in systematic form to students of that subject a summary of our present knowledge of some of the fundamental principles of animal nutrition, particularly from the standpoint of energy relations, with special reference to their bearings upon the nutrition of farm animals."

It is assumed by the author that the reader is already familiar with the general nature of nutrition processes, and he, therefore, devotes all of his energy to that aspect of the subject of nutrition that has been designated by some writers as "the statistics of nutrition." Assuming the existence of a fundamental distinction between matter and energy, the author divides the subject-matter into two parts. The first part deals with the income and expenditure of matter; the second part, with the income and expenditure of energy. The first two chapters of the first part deal quite generally with the essentials of feeding and of metabolism. Then, after devoting a chapter to a consideration of methods, the author discusses the subject of metabolism more minutely under the following heads, to each of which a chapter is devoted: Fasting Metabolism, The Relation of Metabolism to Food-supply, and The Influence of Muscular Exertion upon Metabolism. The plan outlined in the first part is adhered to in the second. After a general consideration in three chapters, of Force and Energy, of the Conservation of Energy in the Animal Body, and of Methods of Investigation, the main subject is developed in detail in the four remaining chapters, entitled: Food as a Source of Energy, Internal Work, Available Energy, and the Utilization of Energy.

The author handles these subjects with great skill. While the well-known facts are usually but briefly illustrated by a few classical experiments, the disputed points are discussed in detail, experiments and statistics are given at great length, together with full references to the literature. These discussions would be rather cumbersome were it not for the fact that each is concluded with a short and accurate summary, bringing all the data into a clear and concise paragraph or table.

The reviewer believes that workers in the field of animal nutrition will find the book of Dr. Armsby very valuable and suggestive, pointing out, as it does, the doubtful and the unknown in this branch of physiology. It is, however, to be regretted that the author adopts the classification of nitrogenous foodstuffs recommended by the Association of American Agricultural Colleges and Experiment Stations. Many of the terms used in this classification have totally different meanings in the classification now generally used by English, German, and American physiologists. J. E.

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ON SUBSTITUTED BENZHYDROL DERIVATIVES AND BROMCYANACETIC ETHER.[1]

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PART I.

On Substituted Benzhydrol Derivatives.

Experiments on the isomeric dibromdiphenylmethanes, $(C_6H_4Br)_2{=}CH_2$, were undertaken with the object of determining, if possible, the position of the two bromine atoms in the benzene rings, and the relative amounts of the different isomers produced when diphenylmethane is brominated at a low temperature. The derivatives of the general formula, $(C_6H_4Br)_2{=}CHX$ (in which $X = Br$, OH, $OCOCH_3$, etc.), were studied with especial care as these compounds are of interest because of their low points of dissociation; they lose HX at temperatures varying from 165° to 300°, and are thus found to be perfectly analogous in their reactions to benzhydrol, benzhydrol ether, diphenylmethyl bromide, and benzylic acid, whose chemistry has been so carefully worked out by Nef.[2]

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[1] The work here described was performed during the years 1895-1897, under the direction of Dr. J. U. Nef, in the Kent Chemical Laboratory of the University of Chicago.

[2] Ann. Chem. (Liebig), 298, 231-256.

Paradibromdiphenylmethane, $(C_6H_4Br)_2{=}CH_2$.—The action of bromine on diphenylmethane has been studied only at high temperatures, when diphenylmethyl bromide[1] is formed. If, however, the action is carried out at low temperatures[2] and in the presence of iodine,[3] the bromine enters the benzene rings exclusively, and *p*-dibromdiphenylmethane (70 per cent) is produced together with small amounts of the corresponding *o,p*- and *o*-dibrom compounds. The exact method of work was as follows: A mixture of diphenylmethane[4] (100 grams) and iodine (10 grams—reaction goes as well with 5 grams) was cooled to 0° in a large flask which was connected with a drop-funnel and with a reflux condenser, the latter being provided with a calcium chloride tube at its upper end. By means of the drop-funnel, 200 grams of bromine (2 mols.) were added drop by drop to the contents of the flask, the latter being shaken constantly. Hydrobromic acid gas was evolved rapidly. When all the bromine had been added, the flask with its contents, which had been kept cold with ice-water, was packed in ice for twelve hours. Subsequently, the very viscous reaction-product was poured into water and the resulting highly colored, heavy oil was extracted with ether. The ethereal solution was washed with sodium hydroxide and then treated with sulphurous acid to remove the iodine, and finally dried over calcium chloride. After distilling off the ether, the residual oil was distilled in a vacuum. It practically all boiled (93 to 96 per cent yield) with slight decomposition at 246°, 47 mm. pressure; at 224°, 22 mm. pressure, or 213°, 16 mm. pressure. The thick, nearly colorless, oily distillate readily solidified in part on cooling. The semi-solid was washed at the filter-pump with cold, low-boiling ligroin, when the oily isomers, consisting of the *o,p*- and probably the *o*-dibrom compounds, dissolved, together with a considerable portion of the crystalline *p*-dibrom compound, which was found to be the chief reaction-product. By distilling off the ligroin from the filtrate and treating the residual oil repeatedly in the manner above described, the latter compound was largely removed from the mixture and was obtained perfectly pure by subsequent recrystallizations from low-boiling ligroin. It was not found possible at this point to separate the *p*-dibrom compound completely from its oily isomers, nor to separate the *o*,*p*- and the *o*-dibromdiphenylmethanes from each other, yet by the oxidation, finally, of the oily mixture to the corresponding ketones, $(C_6H_4Br)_2{=}C{=}O$, and the subsequent separation of these by crystallization, the character of the isomeric products was established (see below).

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[1] Friedel and Balsohn: Bull. soc. chim., **33**, 339, 589; Nef: Ann. Chem. (Liebig), **298**, 232.

[2] Jackson and Field: This JOURNAL, **2**, 10.

[3] Beilstein: Ann. Chem. (Liebig), **143**, 370.

[4] Friedel and Crafts: Ann. chim. phys. [6], **1**, 478; Nef: Ann. Chem. (Liebig), **298**, 231; Radiewanski: Ber. d. chem. Ges., **27**, 3236.

Paradibromdiphenylmethane, whose constitution as a *p*-compound was proved by its conversion into *p*-dibrombenzophenone (see below), is a white, crystalline compound. It is very soluble in ether, alcohol, benzene, glacial acetic acid, acetone, acetic ether, and carbon bisulphide. It is difficultly soluble in cold, low-boiling ligroin; hence this is the best solvent for its purification. After recrystallizing several times and subsequent drying in a vacuum over concentrated sulphuric acid, it melts sharply at 64°.

0.2025 gram substance gave 0.3568 gram CO_2 and 0.0635 gram H_2O.

0.2022 gram substance gave, by the Carius method, 0.2320 gram AgBr.

	Calculated for $(C_6H_4Br)_2{=}CH_2$.	Found.
C	47.85	48.04
H	3.06	3.48
Br	49.07	49.08

Paradibromdiphenylmethyl Bromide, $(C_6H_4Br)_2{=}CHBr$.—This compound was obtained by treating *p*-dibromdiphenylmethane with bromine at 150°.[1] The process was carried out with an apparatus similar to the one already described for the preparation of dibromdiphenylmethane. To *p*-dibromdiphenylmethane, heated to 150°, bromine (slightly more than 1 mol.) was added drop by drop, the containing flask being constantly shaken. Hydrobromic acid gas was evolved vigorously, and when all the bromine had been added the reaction was practically over. When cold, the light-brown, crystalline mass was broken up and water was added. The crystals were filtered off, thoroughly washed with water, dried, and then purified by recrystallizing from ether, or from ligroin, or from a mixture of the two.

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[1] Friedel and Balsohn: Bull. soc. chim., 33, 339.

It should be noted here that the mother-liquors left from the purification of *p*-dibromdiphenylmethyl bromide invariably gave off hydrobromic acid gas, no matter how carefully the ether or ligroin solution had been freed previously from this acid. The mother-liquors also always deposited crystals of *p*-dibrombenzophenone, $(C_6H_4Br)_2{=}C{=}O$ (m. p. 172° to 173°). These crystals, which are long, flat, and thin (sometimes in plates), with obliquely cut ends, possess a pearly luster, and can thus readily be detected among the fine, needle-like crystals of *p*-dibromdiphenylmethyl bromide. They can also be distinguished from the bromide crystals by the fact that they give no reaction with concentrated sulphuric acid, while the latter give a deep-red color with this reagent.

Paradibromdiphenylmethyl bromide is a white, crystalline compound, very soluble in alcohol (by which it is slowly decomposed), benzene, and chloroform; less soluble in ether and ligroin. Hence, the two latter solvents are best used for its purification. It melts at 106° to 107°.

0.2275 gram substance gave 0.3250 gram CO_2 and 0.0538 gram H_2O.

0.1940 gram substance gave, by the Carius method, 0.2680 gram AgBr.

	Calculated for $(C_6H_4Br)_2{=}CHBr$.	Found.
C	38.52	38.96
H	2.22	2.62
Br	59.25	59.09

Paradibromdiphenylmethyl bromide, as well as the corresponding benzhydrol derivatives, gives a deep-red color with concentrated sulphuric acid.[1] It cannot be distilled even under diminished pressure because of its very low point of dissociation. On heating the compound to 165° in absence of air, hydrobromic acid escapes and *p*-tetrabromtetraphenylethylene, $(C_6H_4Br)_2{=}C{=}C{=}(C_6H_4Br)_2$, is formed. When heated above its melting-point in a stream of dry air, it is largely oxidized to *p*-dibrombenzophenone, $(C_6H_4Br)_2{=}C{=}O$. If treated with water under proper conditions, *p*-dibrombenzhydrol ether, $(C_6H_4Br)_2{=}CH{-}O{-}CH{=}(C_6H_4Br)_2$, is produced. Treatment with sodium acetate leads to the formation of *p*-dibrombenzhydrol acetate,

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[1] Nef: Ann. Chem. (Liebig), 298, 241.

$$(C_6H_4Br)_2{=}CH{-}O{-}CO{-}CH_3,$$

while with sodium ethylate or with ethyl alcohol, *p*-dibrombenzhydrol ethyl ether,

$$(C_6H_4Br)_2{=}CH{-}O{-}C_2H_5,$$

results. All these reactions are self-evident from the standpoint of a methylene dissociation.[1]

Two attempts to isolate *p*-dibromdiphenylmethylene bromide, $(C_6H_4Br)_2{=}CBr_2$, through treating *p*-dibromdiphenylmethyl bromide with bromine (1 mol.) at 150°, were unsuccessful. On treating the reaction-product with water, *p*-dibrombenzophenone (m. p. 172° to 173°) was obtained quantitatively. Friedel and Balsohn[2] report that they were unable to purify the corresponding diphenylmethane dibromide, $(C_6H_5)_2{=}CBr_2$, and state that it gave benzophenone when heated to 150° with water. Apparently, *p*-dibromdiphenylmethylene bromide is so unstable that when it is merely brought into contact with water it is decomposed in an analogous manner.

Paradibrombenzophenone, $(C_6H_4Br)_2{=}CO$.—This compound was repeatedly produced in small quantities as a side-product in the experiments on *p*-dibromdiphenylmethane and its derivatives. A carbon and hydrogen analysis of this ketone was carried out when it was obtained as a decomposition-product through heating *p*-dibrombenzhydrol (see below), and it was analyzed for bromine when it was formed as a decomposition-product through heating *p*-dibrombenzhydrol ethyl ether (see below). The results of these analyses are here given:

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[1] Nef: *Ibid.*, **298**, 231-241.

[2] Bull. soc. chim., **33**, 337-339.

0.2047 gram substance gave 0.3441 gram CO_2 and 0.0450 gram H_2O.

0.2690 gram substance gave, by the Carius method, 0.2967 gram AgBr.

	Calculated for $(C_6H_4Br)_2{=}CO$.	Found.
C	45.88	45.84
H	2.33	2.44
Br	47.05	47.18

This ketone was obtained quantitatively by oxidation of *p*-dibrombenzhydrol, $(C_6H_4Br)_2{=}CHOH$, by means of chromic acid. To a weighed quantity of this alcohol (see below) dissolved in glacial acetic acid, the calculated quantity of finely powdered potassium bichromate was added gradually, and the mixture heated for some time. The oxidation was known to be complete when a drop of the solution no longer gave a red color with concentrated sulphuric acid. On addition of water, a crystalline compound was precipitated, which, when filtered, washed, dried, and recrystallized from ligroin, showed the characteristic, slender, flat crystals which have been described above. It melted at 172° to 173°, and it gave no red color with concentrated sulphuric acid. This ketone was likewise quantitatively produced by oxidizing *p*-dibromdiphenylmethane in glacial acetic acid solution with chromic acid.

That the compound produced in all these reactions is *p*-dibrombenzophenone, is proved by its identity with *p*-dibrombenzophenone which has been prepared in other ways by E. Hofmann,[1] by Schöpf,[2] and by Cathcart.[3] The compound obtained in the present case was, furthermore, converted into the oxime (following Schäfer's[4] method for the preparation of *p*-monobrombenzophenone oxime), and a compound melting at 150° to 152° was obtained.[5] This oxime, when crystallized from ligroin, appeared in two distinct forms, each melting sharply at 150° to 152°. One modification consisted of long, slender, needle-like crystals[1] and the other of flat, rhombic ones. When the latter were redissolved in ligroin and the solution "seeded" with the needle-like crystals, all of the compound was obtained in the form of needles, with the melting-point 150° to 152°. These two crystalline forms of this oxime have not been previously mentioned.

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[1] Ann. Chem. (Liebig), **264**, 162.

[2] Ber. d. chem. Ges., **24**, 3767.

[3] *Ibid.*, **25**, 3302.

[4] Ann. Chem. (Liebig), **264**, 154.

[5] Cathcart: Ber. d. chem. Ges., **25**, 3202.

When *p*-dibrombenzophenone was reduced in acid solution, some *p*-dibrombenzhydrol (m. p. 115° to 116°) was obtained, and also a crystalline compound (m. p. 158° to 161°), which may have been the corresponding pinacone,[2] was isolated, but this was not further investigated.

Orthoparadibrombenzophenone, $(C_6H_4Br)_2{=}CO$.—The isomeric dibromdiphenylmethanes obtained by brominating diphenylmethane at a low temperature, consist, as stated above, of about 70 per cent of the crystalline *p*-dibrom compound; about 27 per cent is the *o,p*-compound, while the remainder is probably the *o*-dibrom derivative. This was proved as follows: A mixture of 150 grams of the oily dibromdiphenylmethanes, from which the *p*-compound had been removed as completely as possible in the manner already described, was transformed successively in a manner analogous to that described for the conversion of *p*-dibromdiphenylmethane into the corresponding bromides, $(C_6H_4Br)_2{=}CHBr$, then into the acetates, $(C_6H_4Br)_2{=}CH{-}O{-}CO{-}CH_3$, and into the alcohols, $(C_6H_4Br)_2{=}CH{-}OH$. As none of these compounds could be obtained in a crystalline condition, the alcohols were finally oxidized to the corresponding ketones by means of chromic acid in glacial acetic acid solution. Thus, a mixture of 90 grams of oily ketones was obtained from which 7 grams of *p*-dibrombenzophenone (m. p. 170° to 172°) separated out on cooling. These oily ketones boiled smoothly at 226° and 14 mm. pressure; under considerable decomposition at 323°, ordinary pressure. After some weeks' standing in a cool place, a crystalline compound (60 grams) was deposited slowly and was separated by filtration. This compound, when recrystallized from low-boiling ligroin, appeared in groups of large, flat crystals having squarely cut ends, and melted at 50° to 52°. That this body is identical with *o*,*p*-dibrombenzophenone obtained by Heidenreich[1] from *o*-brombenzoyl chloride and brombenzene in presence of aluminium chloride, was proved by converting a portion of it into its oxime (m. p. 140° to 142°); this oxime was thereupon converted into the corresponding indoxazene compound, which crystallizes in white needles (m. p. 132° to 133°). These transformations were carried out according to Heidenreich's method. The melting-points and other properties of the compounds produced correspond to those given by this investigator.

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[1] Hofmann: Ann. Chem. (Liebig), 264, 164.

[2] Linnemann: *Ibid.*, 133, 27.

A bromine determination of the *p*-bromphenyl indoxazene obtained gave the following figures:

0.1538 gram substance gave, by the Carius method, 0.1053 gram AgBr.

	Calculated for $C_{13}H_8BrNO$.	Found.
Br	29.19	29.25

An attempt was made to obtain *o*,*p*-dibrombenzhydrol by reducing *o*,*p*-dibrombenzophenone with sodium amalgam. The experiment was carried out as in the reduction of the *p*-dibrom ketone, but instead of obtaining the *o*,*p*-dibrombenzhydrol sought, a partial elimination of the bromine was effected. Through a quantitative examination of the solution in which the reduction had been carried out, it was proved that 11 per cent of the bromine had been removed from the weight of *o*,*p*-dibrombenzophenone used.

It seemed probable that the oil from which the *o*,*p*-dibrombenzophenone crystals had been separated must be the corresponding *o*-dibrom ketone. But when an attempt was made to form its oxime, a crystalline compound (2.7 grams out of a possible 5.3 grams) which melted at 140° to 141° was obtained. This body, when heated with sodium ethylate in a sealed tube, gave an indoxazene which melted at 128° to 129°.

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[1] Ber. d. chem. Ges., 27, 1453.

As these melting-points correspond so closely with those of *o*,*p*-dibrombenzophenone oxime and of *p*-bromphenyl indoxazene, respectively, it must be inferred that at least 50 per cent of the oil consisted of *o*,*p*-dibrombenzophenone.

Paratetrabromtetraphenylethylene, $(C_6H_4Br)_2{=}C{=}C{=}(C_6H_4Br)_2$.—It has been stated already that when *p*-dibromdiphenylmethyl bromide is heated hydrobromic acid escapes, and if no air is present *p*-tetrabromtetraphenylethylene is formed quantitatively, as follows:

$$\begin{aligned} 2(C_6H_4Br)_2 : CHBr \;\longrightarrow\; & 2(C_6H_4Br)_2 : C\rightrightarrows \\ & + 2HBr \;\longrightarrow\; (C_6H_4Br)_2 : C : C : (C_6H_4Br)_2 + 2HBr. \end{aligned}$$

If, however, air is present, the methylene derivative may be partially or entirely oxidized to the ketone:

$$\begin{aligned} (C_6H_4Br)_2 : CHBr + O \;\longrightarrow\; & (C_6H_4Br)_2 : C\rightrightarrows \\ & + O + HBr \;\longrightarrow\; (C_6H_4Br)_2 : C : O + HBr. \end{aligned}$$

Thus, when a stream of dry air was drawn through molten *p*-dibromdiphenylmethyl bromide, not more than half the resulting product consisted of the polymerized ethylene derivative, while the remainder was *p*-dibrombenzophenone (m. p. 172° to 173°). This explains why solutions containing *p*-dibromdiphenylmethyl bromide oxidize spontaneously on standing at the ordinary temperature, with loss of hydrobromic acid, to the corresponding *p*-dibrombenzophenone.

It was found that *p*-tetrabromtetraphenylethylene was formed most smoothly when *p*-dibromdiphenylmethyl bromide was heated in a distilling-bulb so arranged that a stream of dry air was drawn through the neck and arm of the bulb, but not through the molten bromide. Under these conditions, the bromide begins to lose hydrobromic acid gas as soon as the temperature of the bath reaches 165°. The temperature was finally raised to 230°–240° and kept there for some hours. The resulting deeply colored residue was dissolved in benzene and thoroughly digested with animal charcoal. Finally the benzene was distilled off and the residue dissolved in hot alcohol; on cooling, tiny, white, needle-like crystals separated out. The presence of any *p*-dibrombenzophenone was readily detected by examination of the first crystals which appeared, and this body was removed mechanically if found. The ethylene derivative, after several recrystallizations from glacial acetic acid, and careful drying for some days in a vacuum over fused caustic potash, melted sharply at 248°.

0.2378 gram substance gave 0.4174 gram CO_2 and 0.0559 gram H_2O.

	Calculated for $(C_6H_4Br)_2=C=C=(C_6H_4Br)_2$.	Found.
C	48.14	47.87
H	2.47	2.61

A molecular weight determination by the freezing-point method, using benzene as a solvent, gave the following results:

	I.	II.
Weight of benzene	30 grams	30 grams
" " compound	0.2110 grams	0.3810 grams
Depression of freezing-point	0°.055	0°.110
Molecular weight found	638.1	577.3
" " calculated for $(C_6H_4Br)_2 : C : C : (C_6H_4Br)_2$		648

An attempt to form the corresponding ethane derivative through reduction of this ethylene compound by means of zinc and acetic acid was unsuccessful. The original ethylene compound (m. p. 248°) was entirely recovered. This compound also refuses to take up bromine.

Paratetrabromtetraphenylethylene is possibly also one of the decomposition-products of *p*-dibrombenzhydrol through heat (see below).

Paradibrombenzhydrol Acetate, $(C_6H_4Br)_2=CH—O—CO—CH_3$. — When *p*-dibromdiphenylmethyl bromide is treated with sodium acetate (1.5 mols.) in glacial acetic acid solution, the corresponding *p*-dibrombenzhydrol acetate is formed.[1] Five such experiments with quantities of the bromide varying from 5 grams to 23 grams were carried out, and in each case nearly quantitative yields were obtained by heating only a few minutes on an asbestos plate under a reflux condenser in order to complete the reaction.

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[1] Friedel and Balsohn: Bull. soc. chim., **33**, 338; Vincent: *Ibid.*, **35**, 304.

On addition of water, an oil separated out, which was extracted with ether, washed with an alkali, and dried over calcium chloride. The ether was distilled off and the oily residue was dissolved in hot ligroin; on cooling, very short, fine, needle-like crystals, which melted at 70° to 72°, were obtained. The compound burned with some difficulty but a carbon and hydrogen analysis gave the following results:

0.2077 gram substance gave 0.3532 gram CO_2 and 0.0645 gram H_2O.

	Calculated for $(C_6H_4Br)_2{=}CH{-}O{-}CO{-}CH_3$.	Found.
C	46.87	46.38
H	3.12	3.44

Paradibrombenzhydrol acetate is very soluble in most organic solvents, but less so in low-boiling ligroin. With concentrated sulphuric acid, it gives the characteristic deep-red color given by the bromide under similar conditions. When heated with water or with alcoholic potash it gives *p*-dibrombenzhydrol.

Paradibrombenzhydrol, $(C_6H_4Br){=}CHOH$.—This compound was best prepared by the action of alcoholic potash (1.5 mols.) upon *p*-dibrombenzhydrol acetate. The reaction was completed in the cold after standing a few hours, or on heating, in a few minutes. A small amount of *p*-dibrombenzophenone usually crystallized out from this alcoholic solution and was separated by filtration. The alcoholic filtrate, when poured into water, gave a fine, white, crystalline precipitate of *p*-dibrombenzhydrol, which was purified by recrystallizing from a mixture of ether and ligroin. Very long, fine, white needles, melting at 115° to 116°, were obtained.

0.2007 gram substance gave 0.3335 gram CO_2 and 0.0574 gram H_2O.

	Calculated for $(C_6H_4Br)_2{=}CHOH$.	Found.
C	45.61	45.32
H	2.92	3.17

Paradibrombenzhydrol was also obtained by the action of water in slightly diluted acetic acid solution upon *p*-dibrombenzhydrol acetate.

Paradibrombenzhydrol is very soluble in ether, alcohol, and acetic acid, but very little soluble in ligroin. When ground in an agate mortar, it shows remarkable electric properties. With concentrated sulphuric acid it gives the characteristic deep-red color already mentioned. When treated with ethyl alcohol in presence of concentrated sulphuric acid, *p*-dibrombenzhydrol ethyl ether is formed, while with benzene in presence of the same acid, *p*-dibromtriphenylmethane results. Both of these compounds will be described below. With oxidizing agents, *p*-dibrombenzophenone is produced.

Paratetrabromtetraphenylethane, $(C_6H_4Br)_2{=}CH{-}CH{=}(C_6H_4Br)_2$.—The behavior of benzhydrol at its dissociation-point (300°) has been thoroughly investigated by Nef.[1] The following experiments show that when *p*-dibrombenzhydrol is heated to its dissociation-point (162°), analogous reactions take place, except that in one case a fair amount of *p*-tetrabromtetraphenylethylene was also obtained.

a. Paradibrombenzhydrol (4 grams), when heated in a distilling-bulb in a metal-bath, began to give off water at 162°. The temperature of the bath was gradually raised to 250°, when the reaction was complete. The fused mass, on heating to 300° for five minutes longer, grew dark in color, therefore the operation was discontinued. The mass was digested with hot benzene, which left a portion insoluble in ether, alcohol, glacial acetic acid, carbon bisulphide, acetic ether, acetone, chloroform, carbon tetrachloride, but soluble in hot nitrobenzene. On recrystallizing from this solvent, a compound (1.5 grams), which melted above 300° and which gave no color-reaction with concentrated sulphuric acid, was obtained. An analysis proved this body to be *p*-tetrabromtetraphenylethane.

0.1961 gram substance gave 0.3442 gram CO_2 and 0.0531 gram H_2O.

0.1938 gram substance gave, by the Carius method, 0.2224 gram AgBr.

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[1] Ann. Chem. (Liebig), 298, 241.

	Calculated for $(C_6H_4Br)_2{=}CH{-}CH{=}(C_6H_4Br)_2$.	Found.
C	48.00	47.87
H	2.77	3.00
Br	49.23	49.09

On examination, the benzene solution, decolorized by digesting with animal charcoal, was found to contain a crystalline compound little soluble in alcohol, from which it was recrystallized till pure. Glistening, flat, slender crystals (0.9 gram), which melted at 172° to 173°, were obtained. This compound, through its properties and analysis (see above), was proved to be *p*-dibrombenzophenone.

The mother-liquors left from recrystallizing *p*-dibrombenzophenone were found to contain a small amount of a crystalline compound melting at 85°—probably a mixture of *p*-dibromdiphenylmethane and *p*-dibrombenzophenone.

b. Paradibrombenzhydrol (2 grams) was placed in a distilling-bulb connected with a U-tube, and a stream of dry air was drawn through the apparatus, while the metal-bath was heated quickly to 250° and kept there for five minutes. Water condensed in the delivery-tube and in the U-tube. The white, crystalline residue was extracted with ether. After adding ligroin and distilling off the ether, hexagonal, transparent crystals of *p*-dibrombenzhydrol ether (see below), melting at 150° to 152°, were deposited.

c. Paradibrombenzhydrol (5 grams) was heated for forty minutes (bath at 300°) in a distilling-bulb provided with a thermometer, and so arranged that a distillate and any evolved gas could be collected. Water distilled off, but no gas was obtained. The crystalline residue was completely dissolved in hot benzene. On distilling off this benzene and redissolving in alcohol, the following compounds were separated by fractional crystallization: *p*-Dibrombenzophenone (1.5 grams) melting at 172° to 173°, *p*-dibromdiphenylmethane (0.4 gram) melting at 63° to 64°, and a compound (0.4 gram) melting at 252° to 254°, which, from its small, needle-like crystals, its solubilities and its melting-point (though this was slightly higher than that given above for the pure substance), was thought to be *p*-tetrabromtetraphenylethylene.

d. In a small flask through which a stream of dry carbon dioxide was constantly drawn and which was arranged under a reflux condenser, *p*-dibrombenzhydrol (5 grams) was heated to 300° for eight hours. The resulting crystalline residue was nearly all dissolved in hot alcohol, and from this solution the following compounds were separated by fractional crystallization: *p*-Dibrombenzophenone (0.6 gram) melting at 172° to 173°, a trace of the body described under *c*, melting at 250° to 254°, also mixtures melting from 120° to 170°, from 170° to 230°, from 160° to 164°. The small residue insoluble in alcohol, left in the bulb, melted at 275°, but there was not a sufficient amount for further purification. It is probable that *p*-dibrombenzophenone, *p*-dibrombenzhydrol ether, possibly *p*-tetrabromtetraphenylethylene, and the corresponding ethane derivative were present in these mixtures, but this was not proved.

Paradibrombenzhydrol Ether, $(C_6H_4Br)_2{=}CH{-}O{-}CH{=}(C_6H_4Br)_2$.—The experiments just described prove that when *p*-dibrombenzhydrol is heated, *p*-dibrombenzhydrol ether is first formed, but since this ether has a dissociation-point only very slightly higher than its alcohol, it cannot, therefore, be isolated in quantity by this process. The best method for the preparation of this compound is to heat *p*-dibromdiphenylmethyl bromide with water.[1] Five grams of the bromide with 20 cc. of water and the amount of calcium carbonate necessary to destroy the hydrobromic acid formed, were heated in a sealed tube at 120° for twenty hours. The residue, which was insoluble in water, was recrystallized from low-boiling ligroin. Two compounds crystallized out, and these were separated mechanically. One (3.35 grams) consisted of masses of short crystals radiating from a center and melting at 148° to 150°; the other (0.2 gram consisted of the long, slender, flat crystals of *p*-dibrombenzophenone, melting at 172 to 173°. On recrystallizing the main reaction-product from ligroin, and finally from alcohol, it melted at 155° to 156°.

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[1] Nef: Ann. Chem. (Liebig), 298, 232.

0.2248 gram substance gave 0.3834 gram CO_2 and 0.0577 gram H_2O.

0.2152 gram substance gave, by the Carius method, 0.2426 gram AgBr.

	Calculated for $(C_6H_4Br)_2{=}CH{-}O{-}CH{=}(C_6H_4Br)_2$.	Found.
C	46.84	46.51
H	2.70	2.85
Br	48.04	48.18

Paradibrombenzhydrol ether is extremely soluble in benzene and in chloroform; less so in alcohol, ether, and ligroin. It gives a deep-red color with concentrated sulphuric acid. That it is not acted upon by boiling with alcohol was proved by heating it (1 gram) with alcohol (15 cc.) in a sealed tube at 100° for thirty hours. The compound was entirely recovered unchanged. On the other hand, heating with acetic acid, very readily converts it, as well as the corresponding *p*-dibrombenzhydrol, into *p*-dibrombenzhydrol acetate—a fact which, in view of the low point of dissociation of both this ether and its alcohol, is easily understood.

Paradibrombenzhydrol Ethyl Ether, $(C_6H_4Br)_2{=}CH{-}O{-}C_2H_5$.—This compound was formed by allowing an alcoholic solution of *p*-dibromdiphenylmethyl bromide to stand in the cold; but the bromide, in the presence of a molecular quantity of cold alcoholic sodium ethylate reacted almost instantly. To insure complete reaction, the mixture was heated a short time; on pouring it into water, an oil separated out which was extracted with ether. This was well washed and then dried over calcium chloride. After distilling off the ether, the residual oil, when distilled in a stream of carbon dioxide, boiled at 228° at 16 mm. pressure. All attempts to distil this oil in presence of air, even under diminished pressure, resulted in the formation of some *p*-dibrombenzophenone.

0.2642 gram substance gave 0.4685 gram CO_2 and 0.0967 gram H_2O.

0.3650 gram substance gave, by the Carius method, 0.3692 gram AgBr.

	Calculated for $(C_6H_4Br)_2{=}CH{-}O{-}C_2H_5$.	Found.
C	48.64	48.36
H	3.78	4.06
Br	43.24	43.25

Paradibrombenzhydrol ethyl ether is a thick, colorless oil with a characteristic, not unpleasant, odor. With concentrated sulphuric acid it gives a deep-red color.

That *p*-dibrombenzhydrol ethyl ether can also be obtained from *p*-dibrombenzhydrol or its corresponding ether, by means of ethyl alcohol and concentrated sulphuric acid, was proved by experiment. This reaction is self-evident, in view of the experiments of Linnemann[1] and Nef,[2] and in view of the low dissociation-point of these substances.

Behavior of p-Dibrombenzhydrol Ethyl Ether on Heating.— Paradibrombenzhydrol ethyl ether has a low dissociation-point. It breaks down at 300° into ethyl alcohol, ethylene (?), *p*-dibrombenzophenone, and *p*-dibromdiphenylmethane. The ether (6.5 grams), placed in a small distilling-bulb which was connected with a second distilling-bulb (receiver) and an azotometer, was heated in a metal-bath to 300° for three hours, when the reaction was complete. A small amount of liquid (b. p. 110°) distilled into the receiver, and at the same time 120 cc. of gas were collected in the azotometer. This gas, which burned with a smoky flame, was probably ethylene. The distillate separated into two layers, one, a a thin liquid, which, when redistilled, came over between 65° to 78° and gave the iodoform test, and was, therefore, probably ethyl alcohol; the other, an oil which had a wintergreen odor and which completely decomposed when an attempt was made to redistil it. The highly-colored crystalline residue left in the distilling-bulb was dissolved entirely in benzene and the solution was decolorized by digesting with animal charcoal. After distilling off the benzene, the residue was dissolved in alcohol. From this solution *p*-dibrombenzophenone (2 grams), melting at 172° to 173°, and *p*-dibromdiphenylmethane (0.6 gram), melting at 62° to 64°, were separated by fractional distillation; the melting-points are those obtained after recrystallizing from low-boiling ligroin.

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[1] Ann. Chem. (Liebig), **133**, 17.

[2] *Ibid.*, **298**, 255.

The result of a bromine determination of the *p*-dibrombenzophenone here obtained has been given above.

Paradibromtriphenylmethane, $(C_6H_4Br)_2{=}CH{-}C_6H_5$. — Paradibrombenzhydrol, treated with benzene and concentrated sulphuric acid, gives *p*-dibromtriphenylmethane.[1] A solution of *p*-dibrombenzhydrol (3 grams) in benzene (50 cc.) was treated with concentrated sulphuric acid (15 cc.). After standing twelve hours in the cold, the highly-colored benzene solution was decanted from the acid, well washed, and then dried over calcium chloride. On distilling off the benzene, a thick oil with a yellowish-green fluorescence was left. It solidified at the end of ten days. The compound distilled without decomposition at 260°, 15 mm. pressure., but still showed a yellowish-green fluorescence. It was found to be remarkably soluble in all organic solvents, but was finally purified by dissolving in alcohol and digesting repeatedly with animal charcoal. The alcoholic solution gave, on adding water, nearly a gram of a compound crystallizing in very fine, almost white, needles, and melting sharply at 100°.

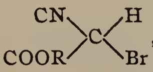
0.2141 gram substance gave 0.4426 gram CO_2 and 0.0687 gram H_2O.

0.1980 gram substance gave, by the Carius method, 0.1850 gram AgBr.

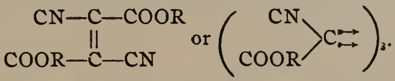
	Calculated for $(C_6H_4Br)_2{=}CH{-}C_6H_5$.	Found.
C	56.71	56.38
H	3.48	3.56
Br	39.80	39.94

PART II.

On Bromcyanacetic Ether, $\begin{matrix}CN\\COOR\end{matrix}{>}C{<}\begin{matrix}H\\Br\end{matrix}$, *and Its Conversion by Loss of Hydrobromic Acid into Dimolecular or Trimolecular Cyanmethylenecarboxylic Ether,*



$$\begin{matrix}CN\\COOR\end{matrix}{>}C{<}\begin{matrix}H\\Br\end{matrix}$$



$$\begin{matrix}CN{-}C{-}COOR\\ \|\\ COOR{-}C{-}CN\end{matrix} \quad \text{or} \quad \left(\begin{matrix}CN\\COOR\end{matrix}{>}C\rightleftarrows\right)_3.$$

The main results of this work on bromcyanacetic ether have already been tabulated briefly by Nef.[1] It has since been sharply proved by him[2] that all primary and secondary alkyl haloids react with various reagents because they are partially dissociated, *i. e.*, alkylidene and HX particles are present, and the speed of the reaction[3] of alkyl haloids depends solely upon the number of such dissociated particles present at a given temperature. Thus, *p*-dibromdiphenylmethyl bromide, whose dissociation-point lies at about 165°, reacts instantly with alcoholic sodium ethylate, or slowly with alcohol, in the cold, whereas ethyl iodide, dissociation-point about 450°, reacts very slowly with alcoholic sodium ethylate in the cold and not at all with alcohol alone at 100°. At 150°, however, ethyl ether is formed.

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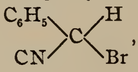
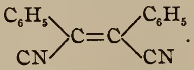
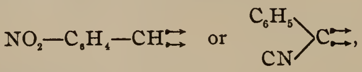
[1] Nef: Ann. Chem. (Liebig), 298, 254.

There are some substituted alkyl haloids, however, as pointed out by Nef,[4] which show a very peculiar behavior when treated with alcoholic sodium ethylate or other so-called double decomposition reagents. Thus, *o*- and *p*-nitrobenzyl chloride give, in marked contrast to benzyl chloride, by treatment with alcoholic potash (or sodium ethylate) no trace of an ether, $NO_2—C_6H_4—CH_2—O—C_2H_5$ (or only small amounts),[5] but quantitative or relatively large amounts of the stilbene derivatives, *o*- and *p*-$NO_2—C_6H_4—CH=CH—C_6H_4—NO_2$. Brombenzyl cyanide,  $(C_6H_5)(CN)C(H)(Br)$, gives, on similar treatment, dicyanstilbene,  $(C_6H_5)(CN)C=C(C_6H_5)(CN)$.

These results can only be understood, as pointed out by Nef, on the basis that the methylene residues, which become free when HX is removed by the alkali,



$$NO_2—C_6H_4—CH\rightrightarrows \quad \text{or} \quad (C_6H_5)(CN)C\rightrightarrows,$$

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[1] Ann. Chem. (Liebig), 298, 258.

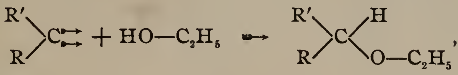
[2] *Ibid.*, 309, 126; 318, 316.

[3] In this way I believe the percentage of dissociation at various temperatures may be determined as accurately as the percentage of ionization of electrolytes by the conductivity method. J. U. NEF.

[4] Ann. Chem. (Liebig), 298, 229, 257-260.

[5] Thiele: *Ibid.*, 305, 103.

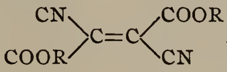
in these cases unite, in part or entirely, with each other to give the olefine derivatives mentioned above; whereas, ordinarily, the alkylidene residues absorb the reagent (alcohol, etc.) set free, or present as such, to give an addition-product,



$$\begin{matrix}R'\\R\end{matrix}\!\!>C\rightleftarrows + HO{-}C_2H_5 \rightarrow \begin{matrix}R'\\R\end{matrix}\!\!>C<\begin{matrix}H\\O{-}C_2H_5\end{matrix}$$

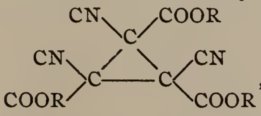
, etc.

Bromcyanacetic ether is another such compound. It gives, as will be seen from what follows, on treatment with sodium, aniline, the sodium salts of malonic ether, and of cyan- and acetoacetic ether, a large amount (up to 67 per cent) of a crystalline compound (m. p. 120° to 122°), which, in view of the facts tabulated above, would naturally be regarded as dicyanfumaric ether, *i. e.*, dimolecular cyanmethylenecarboxylic ether,

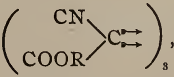


$$\begin{matrix}CN\\COOR\end{matrix}\!\!>C{=}C<\begin{matrix}COOR\\CN\end{matrix}.$$

In 1900, Errara and Perciabosco[1] published a paper on the action of halogens on sodium cyanacetic ether. They found that this ether is converted by iodine, or bromine, into a crystalline compound melting at 119°, and they also obtained the same compound through the action of sodium cyanacetic ether upon bromcyanacetic ether. The compound is obviously identical with that mentioned above and obtained in various ways, as indicated, from bromcyanacetic ether. These observers consider that the compound under discussion is tricyantrimethylenetricarboxylic ether,



, *i. e.*, trimolecular cyanmethylenecarboxylic ester,



$$\left(\begin{matrix}CN\\COOR\end{matrix}\!\!>C\rightleftarrows\right)_3,$$

and this is very probable because of its conversion by saponification and subsequent loss of carbon dioxide[2] into known trimethylene tri- and tetracarboxylic acids. They also give molecular weight determinations confirming this conclusion—which, however, are to be regarded as uncertain[1] (see below).

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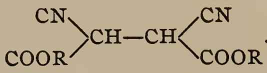
[1] Ber. d. chem. Ges., **33**, 2978.

[2] Scacherl: Ann. Chem. (Liebig), **229**, 89; Büchner: *Ibid.*, **284**, 197.

Finally, it should be mentioned that Thorpe and Young[2] have recently obtained a crystalline substance, melting at 120°, from sodium cyanacetic ether and iodine, to which they give the formula  $\genfrac{}{}{0pt}{}{CN}{COOR}\rangle CH{-}CH\langle\genfrac{}{}{0pt}{}{CN}{COOR}$. This is obviously identical with the dimolecular or trimolecular cyanmethylenecarboxylic ester under discussion. The analytical data given by Thorpe and Young must therefore be erroneous.

Preparation of Bromcyanacetic Ether.—This compound was prepared by adding bromine (1 mol.) slowly to cyanacetic ether which was heated in a bath at 150°, care being taken to avoid access of moisture. The crude reaction-product was distilled directly under reduced pressure. A 60 to 75 per cent yield was obtained.

Bromcyanacetic ether is a colorless oil with a somewhat piercing odor, boiling at 110° to 112°, at 18 mm. pressure, and between 195° to 200° at ordinary pressure, but with considerable decomposition. Treated with aqueous iodide of potassium, iodine is at once set free in the cold—a reaction frequently used as a test for this compound.

0.3348 gram substance gave 0.3839 gram CO_2 and 0.0940 gram H_2O.

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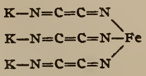
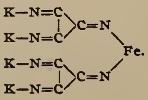
[1] Should further investigations, which I intend to make in the near future, confirm the formula of Errara and Perciabosco, it should be emphasized that this is one of the few instances yet known in which a methylene derivative polymerizes to a trimolecular modification (cf. polymeric fulminic acid, Ann. Chem. (Liebig), **280** 316). Azulmic acid, $(CNH)_x$, the polymerized isocyanides, $(RNC)_x$, the polymeric phenyl- and diphenylmethylenes, $(C_6H_5CH)_x$, $[(C_6H_5)_2C]_x$, are unquestionably all very complex polymers. Finally, I have on the basis of my bivalent carbon work for the past eight years, given in my lectures (cf. also Ann. Chem. (Liebig), **298**, 215, 313) the following very probable formulas to potassium ferri- and ferrocyanide, respectively :





J. U. Nef.

[2] J. Chem. Soc. (London), **77**, 937.

0.3228 gram substance gave 21 cc. N at 18° and 743.7 mm. pressure.

0.1976 gram substance gave, by the Carius method, 0.1923 gram AgBr.

	Calculated for $C_5H_6NO_2Br$.	Found.
C	31.25	31.26
H	3.12	3.11
N	7.29	7.39
Br	41.66	41.41

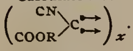
Conversion of Bromcyanacetic Ether into Di- or Tri-molecular Cyanmethylenecarboxylic Ester.

a. By Means of Sodium.—Bromcyanacetic ether in benzene (or ethereal) solution reacted at once in the cold when treated with sodium (1 or 2 mols.) in the form of fine wire. On digesting the salt residue with hot benzene the benzene filtrates gave, on concentration and cooling, a 60 per cent yield of polymeric cyanmethylenecarboxylic ether, melting at 120° to 124°.

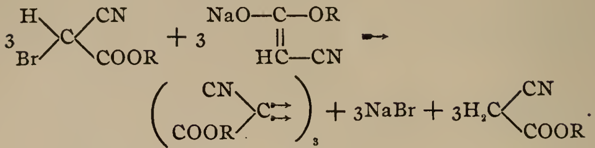
0.2193 gram substance gave 0.4325 gram CO_2 and 0.0905 gram H_2O.

0.2058 gram substance gave 0.4024 gram CO_2 and 0.0871 gram H_2O.

0.2008 gram substance gave 22.5 cc. N at 17° and 747.5 mm. pressure.

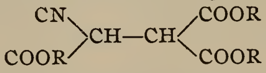
	Calculated for	Found.	
	 $\left(\begin{matrix}CN\\COOR\end{matrix}\!>\!C\begin{matrix}\to\\\to\end{matrix}\right)_x$.	I.	II.
C	54.05	53.78	53.32
H	4.50	4.58	4.70
N	12.61	12.82	....

b. By Means of Sodium Cyanacetic Ether.—Five grams of sodium cyanacetic ether, suspended in absolute ether, were slowly treated in the cold with an ethereal solution of 7.1 grams (1 mol.) of bromcyanacetic ether and the mixture finally heated for four hours under a reflux condenser. Three and two-tenths grams of cyanacetic ether (80 per cent of the theory) boiling at 204°, and 2.7 grams of cyanmethylenecarboxylic ether (67 per cent yield), melting at 120° to 122°, were obtained as reaction-products:



$$3\,{}^{\mathrm{H}}_{\mathrm{Br}}\!>\!\mathrm{C}\!<^{\mathrm{CN}}_{\mathrm{COOR}} + 3\,\begin{matrix}\mathrm{NaO{-}C{-}OR}\\ \|\\ \mathrm{HC{-}CN}\end{matrix} \rightarrow \left({}^{\mathrm{CN}}_{\mathrm{COOR}}\!>\!\mathrm{C}\rightrightarrows\right)_3 + 3\mathrm{NaBr} + 3\mathrm{H_2C}\!<^{\mathrm{CN}}_{\mathrm{COOR}}.$$

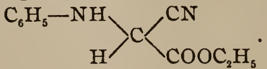
c. By Means of Sodium Acetoacetic Ether and of Sodium Malonic Ether.—These reactions were not carried out quantitatively and therefore need repetition. The operations took place in absolute ethereal solutions and were accomplished, especially in the latter case, with considerable evolution of heat. In the first case the formation of much free acetoacetic ether, as well as of polymeric cyanmethylenecarboxylic ester (40 per cent yield), melting at 120° to 122°, was unquestionably established. In the latter case, some of the polymeric methylene derivative (7 per cent) melting at 120° was isolated. Besides this a small amount of a crystalline compound, volatile with steam and melting at 45° to 47°, which may possibly be



$${}^{\mathrm{CN}}_{\mathrm{COOR}}\!>\!\mathrm{CH{-}CH}\!<^{\mathrm{COOR}}_{\mathrm{COOR}}$$

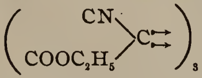
was obtained.

d. By Means of Aniline.—Bromcyanacetic ether and aniline (1.5 mols.), in ethereal solution, reacted on each other in the cold. After standing forty-eight hours, a yield of 25 per cent of the theoretical amount of polymerized cyanmethylenecarboxylic ester (119° to 120°) was obtained. The other products formed, besides phenylammonium bromide, were a substance with odor of bromcyanogen, and a crystalline compound melting at 57°. The latter may possibly be the anilido derivative,



$${}^{\mathrm{C_6H_5{-}NH}}_{\mathrm{H}}\!>\!\mathrm{C}\!<^{\mathrm{CN}}_{\mathrm{COOC_2H_5}}.$$

Properties of Di- or Trimolecular Cyanmethylenecarboxylic Ester.—The crystalline substance formed in all the reactions discussed above melts, when thoroughly purified by crystallizing from benzene, at 122°. It is very sparingly soluble in cold ether and ligroin, and quite soluble in chloroform and hot benzene. Acetone, acetic ether, and especially hot alcohol, dissolve it freely, but gradually act upon it. The molecular weight determinations by the freezing-point method in benzene, given by Errara and Perciabosco,[1] agree with the trimolecular formula



$\left(\begin{matrix}\mathrm{CN}\\ \mathrm{COOC_2H_5}\end{matrix} > \mathrm{C}\rightleftarrows\right)_3$

(theory = 333).

These determinations were repeated with the following results, which agree better with the dimolecular formula (222), and which prove that Errara and Perciabosco worked in one case with a supersaturated solution:

	I.	II.
Weight of substance	0.0963 gram	0.1381 gram
" " benzene	17.4313 "	26.5160 "
Depression of freezing-point	0°.120	0°.116
Molecular weight found	225	220

	III.	IV.
Weight of substance	0.2550 gram	0.3586 gram
" " benzene	26.5160 "	30.6115 "
Depression of freezing-point	0°.182	0°.180
Molecular weight found	258	317

Determinations I. and II. only are reliable, since solutions III. and IV. were proved to be supersaturated as follows: Solution III. was cooled to its freezing-point and maintained at this temperature (as indicated by a Beckmann thermometer) for ten minutes. Thereupon, 10 cc. of the supernatant liquid were transferred to a weighed dish and the following results obtained by evaporation to dryness. Volume of solution = 10 cc.; sp. gr. of benzene at 5° = 0.8885; weight of benzene used = 8.885 grams; weight of solid residue = 0.0826 gram. From these data it is clear that 0.0092 gram of substance dissolve in 1 gram of benzene at 5°. In one of the molecular weight determinations given by Errara and Perciabosco, 0.01157 gram of substance to 1 gram of benzene were used, therefore the solution in this case was supersaturated. In the other molecular weight determination given by them an exactly saturated solution was used.

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[1] Ber. d. chem. Ges., 33, 2981.

In view of these data, molecular weight determinations were carried out by the boiling-point method, using McCoy's apparatus,[1] and the following very curious results were obtained:

	I.	II.
Weight of substance	0.5088 gram	0.6042 gram
Volume of benzene	18 cc.	24.1 cc.
Elevation of boiling-point	0°.210	0°.190
Molecular weight found	441	443
	III.	IV.
Weight of substance	0.6042 gram	0.5676 gram
Volume of benzene	26 cc.	23.7 cc.
Elevation of boiling-point	0°.155	0°.161
Molecular weight found	491	490

The only experimental evidence, therefore, which exists at present in favor of Errara and Perciabosco's trimolecular formula is the conversion of the compound by saponification and subsequent loss of carbon dioxide into known trimethylene derivatives as mentioned above.

In conclusion, the writer wishes to express her most grateful appreciation to Dr. Nef for his kindness, for his numerous suggestions, and for the unvarying patience and constant interest with which he followed the progress of this work.

Contribution from the New York Agricultural Experiment Station.

THE STATUS OF PHOSPHORUS IN CERTAIN FOOD MATERIALS AND ANIMAL BY-PRODUCTS, WITH SPECIAL REFERENCE TO THE PRESENCE OF INORGANIC FORMS.

By E. B. Hart and W. H. Andrews.

The following research forms part of and is preliminary to an extended investigation to be carried on at this station under the direction of Dr. W. H. Jordan on the metabolism of phosphorus and sulphur in the animal body.

It is quite generally believed that phosphorus exists in plant substances, partly in organic combinations as nucleoproteids, nucleins and lecithins, and partly in inorganic forms, such as calcium, magnesium,[1] and potassium phosphates. It is not difficult to understand how this view of the occurrence of phosphorus in vegetable tissue originated, since inorganic combinations form the basis of supply to the growing plant and since it is in the ash that we have chiefly studied the kinds and proportions of the inorganic plant constituents. Starting with the assumption that a considerable proportion of the phosphorus in animal and human vegetable foods is inorganic in form, our efforts have been directed towards the elaboration of a method for separating and quantitatively estimating, at least approximately, this form of phosphorus in vegetable and animal feeding-stuffs.

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[1] This Journal, **23**, 353.

It was also thought that should the ratio of organic to inorganic phosphorus vary greatly in the different vegetable products, this fact might be made the basis of investigations as to the relative nutritive value of these products for specific purposes.

Such investigations could be undertaken, however, only after the evolution of a fairly safe method for the separation of inorganic from organic phosphorus.

Total Phosphorus.

Before taking up the experimental details of the estimates of inorganic phosphorus, determinations of total phosphorus were made on a number of vegetable and animal products by both the magnesium nitrate and the Neumann methods. The Neumann method was tried particularly because it is convenient for use on large volumes of liquids, a condition which must be met in the separations involved in this inquiry.

Magnesium Nitrate Method.—This method is essentially the same as that used by the Association of Official Agricultural Chemists:[2] Five grams of material were well mixed in a platinum dish with 2 to 4 cc. of a solution of magnesium nitrate and incinerated at a low heat. In most cases a perfectly white ash was obtained. This residue was dissolved in dilute hydrochloric acid, made up to 200 cc., an aliquot being taken for the estimation of total phosphorous.

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[1] Sherman: U. S. Dept. Agr., Bull. 121.

[2] Bull. 46, Revised Edition, Bureau Chem., Dept. of Agr.

Neumann Method.—This is the method described by Neumann[1] and already used by Sherman:[2] Five grams of material were placed in a Kjeldahl flask, 10 to 15 cc. concentrated sulphuric acid were added, and the mixture was heated over a low flame until well charred. When partly cooled, 5 to 10 grams of ammonium nitrate were added and the digestion continued. Further additions of ammonium nitrate were made from time to time to entirely oxidize and decolorize the mixture. On cooling, the residue was rinsed into a 200 cc. flask, diluted to the mark, and an aliquot was taken for the determination of total phosphorus by the molybdate-magnesium method. The large amount of ammonium sulphate formed on neutralizing with ammonia seems to impede the precipitation of ammonium phosphomolybdate and only when a generous excess of ammonium molybdate was added—150 cc.—did we get a rapid separation of the yellow precipitate.

Table I.

Substance.	Percentage of phosphorus found in air-dry material.	
	Magnesium nitrate method.	Neumann method.
Corn	0.313	0.310
Oats	0.355	0.339
Wheat bran	1.548	1.537
Malt sprouts	0.677	0.670
Brewer's grains	0.421	0.419
Distiller's grains	0.307	0.303
Linseed meal	0.789	0.787
Oat straw	0.135	0.129
Alfalfa	0.266	0.267
Meat meal	4.073	3.971
Liver meal	1.034	1.029
Dried blood	0.123	0.126
Cow feces	0.344	0.353

The two methods yield practically the same results.

Separation of Organic and Inorganic Phosphorus.

Iwanow[3] has lately studied the changes occurring in the organic phosphorus combinations during the germination of vetch (*Vicia sativa*) and has reached the conclusion that there is a gradual decrease of organic phosphorus with corresponding increase of the inorganic forms as germination proceeds. The seeds were germinated in the dark. The method of separation used by Iwanow was as follows: Five to seven grams of the material were warmed on the water-bath ten to fifteen minutes with 100 to 150 cc. of 1 per cent acetic acid. After cooling, the precipitated proteid matter was separated by filtration through a small flannel filter and washed with water until about 500 cc. filtrate had been collected. For the determination of the inorganic phosphorus, an aliquot from the 500 cc. was taken and precipitated directly with molybdate solution.

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[1] Dubois Reymond's Archiv. (Physiol. Abth.), 1897, pp. 552–553.

[2] J. Am. Chem. Soc., **24**, 1105 (1902).

[3] Ber. d. bot. Ges., **20**, Heft 7 (1902).

Zaleski,[1] working independently and on the same problem, evolved an almost identical method. This investigator recommends the use of either a 1 per cent acetic acid or 0.2 per cent hydrochloric acid solution as the extracting reagent. As will be shown later in both of these methods, the cleavage action on soluble nucleins of the nitric acid contained in the molybdate solution is not sufficiently taken into account. It is true that Zaleski recommends that no extra nitric acid be added, he himself using only the ordinary molybdate solution.

Kossel,[2] working on muscle extracts, has used a mixture of tannin and 5 per cent hydrochloric acid as the precipitant of proteids containing phosphorus.

Araki[3] has recently used this method, somewhat modified, in his studies of the decomposition of nucleic acids by enzymes. The method of Araki is as follows: Two grams of a salt of nucleic acid were dissolved in 40 cc. of water and to this the enzyme was added. This solution was then diluted with an equal volume of water, 4 grams of sodium acetate added, and tannin so long as a precipitate continued to be formed. The filtrate from this precipitate, according to Araki, should contain any free phosphoric acid split off by the action of the enzyme. In our hands, as we shall show later, tannic acid in dilute mineral acid solution and tannic acid with sodium acetate both fail to completely precipitate the soluble nucleins contained in certain of our feeding-materials. We do not assume to deny the accuracy of the results of these authors, recognizing the important fact that the constitution and consequent reaction of the nucleic acids with which these investigators worked may be entirely different from those that occurred in our materials.

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[1] *Ibid.*, **20**, Heft 7 (1902).

[2] Ztschr. physiol. Chem., **7**, 9 (1883).

[3] *Ibid.*, **38**, 84 (1903).

Our preliminary work was done on whole oats, ground and air-dried. Five-gram samples were treated with 125 cc. of the extracting reagent for varying lengths of time, with occasional vigorous shakings. The mixtures were then allowed to settle and the supernatant liquid was decanted through dry filters into 500 cc. flasks. The residue was washed by decantation with several portions of water until 500 cc. of filtrate had been collected. To 200 cc. of this filtrate 10 grams of ammonium nitrate were first added, and after heating the solution to 65° C., 50 cc. of ordinary ammonium molybdate solution were added, the whole kept at 65° C. for fifteen minutes, then removed from the bath and allowed to stand for one hour. The precipitate was then filtered off, washed with a small quantity of water, and the phosphorus estimated as magnesium pyrophosphate. This was supposed to be the inorganic phosphorus. The total soluble phosphorus was determined in another aliquot of 200 cc. by the Neumann method. The phosphorus in the insoluble residue, representing a mixture of nucleoproteids, nucleins, and lecithins, was also determined and designated as insoluble organic phosphorus. Tannin, with acetic and hydrochloric acids, under the conditions shown in the table on the following page, was also tried. The molybdate solution used was one prepared according to the method adopted by the Official Agricultural Chemists.[1]

These results show how decided a variation may occur in the quantities of the different forms of phosphorus as estimated under varying conditions of manipulation. They also

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[1] Bull. 46, Revised Edition, Bureau Chem. Dept. of Agr.

Table II.

Substance.	Acid.	Total phosphorus.	Percentage of phosphorus in air-dry material.		
			Insoluble organic phosphorus.	Soluble phosphorus.	Inorganic phosphorus.
Oats	1 per cent acetic, 12 mm., 55° C.	0.355	0.210	0.142	0.035
	1 " " room temp., 24 hours		0.240	0.116	0.042
	1 " " " " 40 "		0.227	0.138	0.032
	1 " " " " 3 "		0.252	0.103	0.017
	0.2 " hydrochloric, room temp., 40 hours		0.258	0.092	0.006
	0.5 " " 10 mm., 55° C.		0.184	0.171	0.014
	1 " acetic, room temp., 17 hours, tannin		0.094	0.244	Tannin interferes.
	0.2 " hydrochloric, room temp., 17 hours, tannin		0.206	0.126	
	1 " acetic, 10 mm., 55° C., tannin		0.075	0.240	
	0.2 " hydrochloric, 10 mm., 55° C., tannin		0.223	0.109	

show in certain instances an apparent inorganic content appreciably large, while in others practically none was found, indicating again the influence of certain varying factors in the method of separation. That tannin fails to remove a large proportion of soluble organic forms is also very evident.

We next made the same separations with a number of materials, using, as the extracting reagents, 0.2 per cent hydrochloric and 1 per cent acetic acid solutions for forty hours at room temperature. The inorganic phosphorus was estimated by the same method as that used in the case of oats.

Table III.

			Percentage of phosphorus in air-dry material.		
Substance.	Acid.	Total phosphorus.	Insoluble organic phosphorus.	Soluble phosphorus.	Inorganic phosphorus.
Wheat bran	Acetic	1.548	0.111	1.422	1.230
	Hydrochloric		0.428	1.121	0.120
Malt sprouts	Acetic	0.677	0.176	0.479	0.389
	Hydrochloric		0.213	0.477	0.350
Brewer's grains	Acetic	0.421	0.382	0.042	0.005
	Hydrochloric		0.395	0.032	0.006
Distiller's grains	Acetic	0.307	0.229	0.082	0.022
	Hydrochloric		0.244	0.075	0.022
Corn	Acetic	0.313	0.155	0.163	0.017
	Hydrochloric		0.159	0.153	0.015
Alfalfa	Acetic	0.266	0.057	0.205	0.174
	Hydrochloric		0.084	0.189	0.136
Linseed meal	Acetic	0.789	0.470	0.327	0.166
	Hydrochloric		0.564	0.195	0.102
Liver meat meal	Acetic	1.034	0.488	0.618	0.347
	Hydrochloric		0.486	0.585	0.380
Dried blood	Acetic	0.123	0.099	0.020	0.019
	Hydrochloric		0.080	0.042	0.045
Cow feces	Acetic	0.344	0.193	0.159	0.091
	Hydrochloric		0.199	0.141	0.084

It will be noticed from these results that whenever there is a large amount of total soluble phosphorus there is also a corresponding increase in the amount of inorganic phosphorus. In but one instance—that of the hydrochloric acid extract of bran—did this fail to hold true. In all cases, the character of the inorganic precipitate was greatly different from that of an ammonium phosphomolybdate precipitate. It was invariably of a flocculent, proteid-like nature, and only on standing did the characteristic yellow precipitate begin to separate. This certainly indicated a slow cleavage of the organic phosphorus in the solution which was brought about by the excess of nitric acid in the molybdate reagent. In the case of the acetic acid extract from bran, this cleavage was especially marked. Such conditions of manipulation certainly lead to results altogether too high for inorganic phosphorus.

To determine more definitely the point as to whether certain nucleic acids are so easily split up as our results indicated, we made preparations of these bodies from wheat bran and fresh corn-germ meal. That from wheat bran was separated by Osborn's method[1] and gave a product extremely low in phosphorus, less than 1 per cent, and high in proteid matter. The filtrate from the pepsin digestion—a part of the Osborne method—showed an abundance of an easily cleavable organic phosphorus combination. This is in harmony with our other results, that the nucleins or salts of nucleic acid of wheat bran are extremely soluble in dilute acid solutions.

By Levene's method[2] we separated from wheat bran a nucleic acid carrying 7.59 per cent of phosphorus, and from fresh germ meal one containing 6.83 per cent. Both these products were soluble in water, yielding pale-yellow solutions. When dissolved in water and tested as in the above method for the estimation of inorganic phosphorus, that is, with 50 cc. molybdic solution at 65° C. in the presence of ammonium nitrate, a flocculent precipitate first separates. This soon takes on a yellow color and the ammonium phosphomolybdate settles out.

It became apparent that a method estimating, at least approximately, the amount of inorganic phosphorus in our feeding materials and animal by-products, must take into account the amount of free acid in the precipitating reagent. With this point in view, we first established the amount of nitric acid necessary to separate quantitatively ammonium phosphomolybdate when neutral ammonium molybdate was added to a neutral solution of inorganic phosphorus. We found that 2 cc. of nitric acid of sp. gr. 1.20 in 225 cc. of solution would cause quantitative separation in water extracts and in extracts made with 0.2 per cent hydrochloric acid and neutralized with ammonia. In the 1 per cent acetic acid extracts, neutralized with ammonia, 4 cc. of nitric acid of sp. gr. 1.20 are necessary because of the retarding action of the ammonium acetate on the separation of ammonium phosphomolybdate. Ten grams of ammonium nitrate were added to the above volume. Neutral ammonium molybdate was prepared by addition of ammonia to the ordinary molybdate solution, using litmus as an indicator.

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[1] Ann. Rep. Conn. Agr. Exp. Sta., 1901.

[2] J. Am. Chem. Soc., **22**, 239 (1900).

Preliminary estimations showed that forty hours' extraction was entirely unnecessary. Three hours, the time required to thoroughly wash the residue, gave nearly as high total soluble phosphorus as forty hours. In the next table is presented results secured by the following method: Five grams of the sample were vigorously shaken with 125 cc. of the extracting reagent for 15 minutes. The mixture was then allowed to settle, was decanted through a filter-paper into a 500 cc. flask, and the residue washed with water until about 500 cc. of filtrate had been collected. Two hundred cc. of the filtrate were next neutralized with ammonia, using litmus as indicator, and 10 grams of ammonium nitrate added. The solution was then warmed to 65° C. and, in the case of the water and hydrochloric acid extracts, 2 cc. nitric acid (sp. gr. 1.20) and 25 cc. neutral ammonium molybdate were added. To the acetic acid extracts 4 cc. nitric acid (sp. gr. 1.20) were added. The extracts were allowed to stand fifteen minutes at 65°, were then removed from the bath and after one hour were filtered. The phosphorus was estimated as the magnesium salt.

Table IV.

		Percentage of phosphorus in air-dry material.		
Substance.	Treatment.	Total phosphorus.	Total soluble phosphorus.	Inorganic phosphorus.
Oats	Water	0.355	0.180	0.00
	Acetic		0.114	0.00
	Hydrochloric		0.096	0.00
Bran (wheat)	Water	1.548	0.356	0.143
	Acetic		1.100	0.055
	Hydrochloric		0.951	0.036
Malt sprouts	Water	0.677	0.548	0.391
	Acetic		0.489	0.279
	Hydrochloric		0.477	0.017
Brewer's grains	Water	0.421	0.142	0.007
	Acetic		0.039	0.007
	Hydrochloric		0.040	0.009
Distiller's grains	Water	0.307	0.079	0.012
	Acetic		0.104	0.005
	Hydrochloric		0.069	0.007
Corn	Water	0.313	0.276	0.014
	Acetic		0.203	0.00
	Hydrochloric		0.177	0.00
Alfalfa	Water	0.266	0.196	0.064
	Acetic		0.182	0.079
	Hydrochloric		0.180	0.079
Linseed meal	Acetic	0.789	0.327	0.085
	Hydrochloric		0.195	0.088
Oat straw	Acetic	0.135	0.095	0.028
	Hydrochloric		0.086	0.009
Wheat	Water	0.390	0.125	0.028
	Acetic		0.174	0.040
	Hydrochloric		0.172	0.008
Blood	Water	0.123	0.029	0.005
	Acetic		0.028	0.010
	Hydrochloric		0.054	0.00
Meat meal	"	4.073	1.387	0.098
Liver meat meal	"	1.034	0.486	0.005
Cow feces	"	0.344	0.148	0.004

These results clearly show that where the amount of nitric acid used in the determination of inorganic phosphorus was reduced to the minimum, there was a marked decrease in the amount of this form of phosphorus apparently present. This decrease is especially noticeable in the hydrochloric acid extracts. In fact the estimations by the use of hydrochloric acid, with the exceptions of alfalfa and linseed meal, we regard as indicating the absence of inorganic phosphates. The water and acetic acid extracts of bran and malt sprouts show considerably higher figures for inorganic phosphorus than the hydrochloric acid extract. It will be observed that both these materials are rich in easily soluble, organic compounds. That these compounds are more easily split up into inorganic forms by water alone and 1 per cent acetic acid than by 0.2 per cent hydrochloric acid seems a possible explanation of the results secured. Even when bran has been extracted with a 1 per cent solution of hydrochloric acid for forty hours, the inorganic estimation showed but 0.088 per cent, while the total soluble phosphorus was 1.26 per cent. We found it impossible to filter extracts of linseed meal and, consequently, could only prepare such extracts by decantation. This, of course, gave us a distintly turbid solution. On precipitating with molybdate solution, an unusually large, flocculent precipitate resulted, difficult to filter and wash. It redissolved readily in ammonia. Also in the case of alfalfa, a very large, flocculent precipitate was formed on adding the molybdate solution. Later, working with sprouted grains, we estimated in one case as inorganic phosphorus 0.0118 gram magnesium pyrophosphate. This precipitate, after ignition, was unusually white. On dissolving it in dilute nitric acid and reestimating the phosphorus, we weighed but 0.0017 gram of magnesium pyrophosphate. This is an extreme case, but it indicated that where we have a large, flocculent, proteid precipitate with our molybic acid, soluble again in ammonia, there can be formed on the addition of magnesia mixture insoluble proteid-magnesia combinations convertible to magnesium oxide on ignition and weighed as magnesium pyrophosphate. With this precaution in mind, we redetermined the inorganic phosphorus in alfalfa and linseed meal. On the first weighing as magnesium pyrophosphate they showed respectively 0.0072 and 0.0107 gram. On dissolving in dilute nitric acid, we weighed as magnesium pyrophosphate 0.0006 gram and 0.0005 gram, respectively. These figures are equivalent to 0.008 per cent inorganic phosphorus in alfalfa and 0.007 per cent in linseed meal, figures we still believe due to errors of manipulation.

Experiments with the Use of Tannin and Sodium Acetate.

Since Araki has used this method as a means of separating nucleic acids from solutions containing organic and inorganic phosphorus, it was thought that it might be applied to our work. Extracts were made with 0.2 per cent hydrochloric and 1 per cent acetic acids in the usual way. To 200 cc. of the extract, neutralized with ammonia, 12 grams of sodium acetate were added and then a solution of tannin until no further precipitate was formed. The mixture was then diluted to 250 cc., filtered through a dry filter, and in 200 cc. the total phosphorus (supposedly inorganic) determined by the Neumann method. The reagents used were phosphorus free.

Table V.

		Percentage of phosphorus in air-dry material.	
Substance.		Total phosphorus.	Inorganic phosphorus.
Wheat	Water	0.390	0.087
	Acetic		0.147
	Hydrochloric		0.147
Bran	Water	1.548	0.398
	Acetic		1.026
	Hydrochloric		0.783
Distiller's grains	Water	0.307	0.080
	Acetic		0.092
	Hydrochloric		0.063
Malt sprouts	Water	0.677	0.528
	Acetic		0.471
	Hydrochloric		0.483
Brewer's grains	Water	0.421	0.115
	Acetic		0.061
	Hydrochloric		0.026
Oat straw	Water	0.135	0.094
	Acetic		0.061
	Hydrochloric		0.083

These results give further evidence that tannin and sodium acetate could not be used for the separation of organic and inorganic phosphorus in such materials.

Method Adopted.

The method we have finally adopted as giving results nearest the truth is that detailed above for the hydrochloric acid extract of Table IV., with the following modification: After ignition the magnesium pyrophosphate is dissolved in dilute nitric acid and the phosphorus reestimated. This, as detailed above, is to prevent the error of weighing magnesium pyrophosphate contaminated with magnesium oxide. We do not expect the method to give absolute results in all cases. What we claim for it is that it reduces the hydrolyzing action of the reagents to a minimum, but at the same time allows complete precipitation of inorganic phosphates.

In one experiment, when to a solution containing 0.0413 gram of inorganic phosphorus estimated as magnesium pyrophosphate, were added 0.500 gram of nucleic acid prepared from wheat bran, and the solution then subjected to the above treatment, the recovery was 0.0439 gram, a gain of 0.0026 gram by cleavage of the nucleic acid present. This 0.0026 gram of magnesium pyrophosphate calculated in percentage of phosphorus on a 2 gram sample is equal to 0.036 per cent. It can be readily seen, then, that estimations of inorganic phosphorus giving results as high as 0.036 per cent in solutions rich in soluble organic phosphorus can easily be accounted for as coming by cleavage of organic phosphorus compounds.

Attempts have been made to remove the interfering proteids by precipitation with neutral ammonium molybdate in solutions cooled to 18° C. and in the presence of but 1 cc. nitric acid (sp. gr. 1.20) in 250 cc. volume. This did bring about partial removal, but on warming the solutions with the addition of the extra 1 cc. of nitric acid (sp. gr. 1.20), necessary to precipitate the inorganic phosphorus, there was generally a further precipitation of proteid matter and consequent interference.

Experiments with Germinated Grains.

Since Iwanow[1] and Zaleski,[2] working independently, have shown that during the germination in the dark of vetch and lupine, a marked decrease in organic phosphorus with corresponding increase in inorganic forms appeared to take place, it became of interest to carry on similar work, using our own method for the separation of inorganic phosphorus. Both these workers used the ordinary molybdate solution containing free nitric acid in their inorganic determinations. For our work we selected corn, oats, and wheat. These were germinated in pure glass sand in the dark for periods of one and two weeks. At the ends of these periods, the grains were dried at 60° C., separated from the adhering sand, and finely ground. After exposure to the air for a few days the samples were bottled and analysis made by the hydrochloric acid method. Below we give the data, and for comparison, results obtained on the unground seeds. We also present data secured on the two-weeks-old germinated seeds by the Iwanow method. Fifty cc. of ordinary molybdate were used to 200 cc. of extract. Iwanow does not state the exact quantity of molybdic solution which he used, so we are unable to exactly repeat his method.

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[1] Ber. d. bot. Ges., **20**, Heft. 7 (1902).

[2] *Ibid.*, **20**, Heft. 7 (1902).

Table VI.

			Percentage of phosphorus in air-dry material.		
Substance.	**Treatment.**	**Total phosphorus.**	**Total soluble phosphorus.**	**Inorganic phosphorus.**	**Iwanow method. Inorganic phosphorus.**
Wheat	Ungerminated	0.390	0.172	0.008	
	1 week		0.211	0.018	
	2 weeks		0.279	0.031	0.273
Corn	Ungerminated	0.313	0.177	0.00	
	1 week		0.237	0.011	
	2 weeks		0.312	0.036	0.212
Oats	Ungerminated	0.355	0.096	0.00	
	1 week		0.181	0.022	
	2 weeks		0.302	0.032	0.217

We see from the above figures that during the germination of these seeds in the dark there is a marked increase in soluble organic phosphorus compounds, but that according to our method of estimation the cleavage does not extend to the formation of inorganic phosphates. The increase of inorganic phosphorus accompanying the increase of total soluble organic phosphorus is explained by the slight cleavage action of our reagents.

The Iwanow[1] method in our hands gives results in perfect agreement with his previously reported results—that is, that during germination in the dark there is a marked formation of inorganic phosphorus.

The discrepancy in the two results appears to be due to differences of method. Araki,[2] working on the action of certain enzymes, as pepsin, trypsin, and erepsin, and on nucleic acids of animal origin, came to the conclusion that the structure of these bodies was but little disturbed by the action of these enzymes.

Our results bring us to the conclusion that during germination there is a proteolysis of nucleoproteids with formation of more soluble mobile nucleins and nucleic acids, but not a transformation of the organic phosphorus into the inorganic.

Summary.

(1) Our commercial feeding-stuffs of vegetable origin do not contain appreciable quantities of phosphorus in inorganic combination.

(2) The animal feeding-materials, such as liver meal and dried blood, when representative, are also approximately free from this form of phosphorus. Commercial meat meal, liable to carry varying quantities of bone, does contain inorganic phosphorus, dependent, of course, on the amount of bone present. The feces of the cow used in our experiment are also free from inorganic phosphorus.

(3) Germinated grains are rich in forms of soluble organic phosphorus.

(4) Germination, extending over a period of two weeks, on oats, corn, and wheat, did not transform organic phosphorus into inorganic forms.

[1] *Loc. cit.*

[2] Ztschr. physiol. Chem., 38, 84 (1903).

In conclusion, we wish to express to Dr. Jordan, at whose instigation this work was undertaken as preliminary to studies on phosphorus and sulphur metabolism in animals, and to Dr. Van Slyke, our sincere thanks for their constant interest and many helpful suggestions.

THE CHLORIDES OF PARABROMORTHOSULPHOBENZOIC ACID AND SOME OF THEIR DERIVATIVES.[1]

BY WILLIAM M. BLANCHARD.

PART I.

The interesting results obtained in the study of the chlorides of orthosulphobenzoic acid[2] and the chlorides of paranitroorthosulphobenzoic acid[3] led to an investigation of the chlorides of parabromorthosulphobenzoic acid. The work was undertaken by Edward S. Smith at the suggestion of Professor Remsen. Smith prepared a large quantity of pure acid potassium salt of parabromorthosulphobenzoic acid from which he obtained the mixed chlorides. By treating a portion of the mixed chlorides with ammonia he isolated the symmetrical chloride, and by fractional crystallization of another portion, he obtained several crystals of the unsymmetrical chloride in pure condition.

At this point Smith left the university, and it was with the material that he had prepared, and at Professor Remsen's suggestion, that the present author took up the work.

Soon after the work was begun, greater interest was given to it by the appearance of an article by List and Stein,[4] in which it was stated that several of the conclusions in the papers already referred to were erroneous, that the two chlorides furnish an interesting case of tautomerism, that each individual chloride reacts at one time as a symmetrical, and at another time as an unsymmetrical compound, and that it is not possible to determine with certainty the constitution of either chloride by means of chemical investigation.

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[1] From the author's dissertation submitted, June, 1900, to the Board of University Studies of the Johns Hopkins University, in conformity with the requirements for the degree of Doctor of Philosophy.

[2] This JOURNAL, **17**, 330, 347; **18**, 794, 809, 819.

[3] *Ibid.*, **19**, 496.

[4] Ber. d. chem. Ges., **31**, 1648.

The experimental part of this work will now be presented, after which some remarks will be made upon the conclusions to be drawn therefrom.

Acid Potassium Salt of Parabromorthosulphobenzoic Acid.—The material that formed the basis of this work was parabromtoluene. This was obtained in crystalline form, melting at about 32° to an almost colorless liquid. It was sulphonated and oxidized by a method differing but slightly from that described by Hübner and Post.[1] To the parabromtoluene in a large flask fuming sulphuric acid was added in the proportion of 5 parts by weight of acid to 2 parts by weight of bromtoluene, the acid being added in small portions and the temperature kept down to about 40°, by placing the flask in cold water when necessary. The reaction was complete in an hour. The clear, dark-brown solution was poured into about ten times its volume of cold water, the excess of sulphuric acid neutralized with calcium carbonate, and the precipitated calcium sulphate removed by filtration. The filtrate was heated to boiling, a slight excess of potassium carbonate added, and the boiling continued for at least an hour to insure the complete conversion into the carbonate of all the magnesium, which is usually found to some extent in commercial calcium carbonate. When this precaution was not observed, it was found extremely difficult to separate and purify the salt desired. The precipitated calcium and magnesium carbonates were filtered off and the filtrate evaporated to a smaller volume, when, on cooling, a large quantity of crystals was obtained. By fractional crystallization, these were separated into two salts, potassium parabrommetatoluenesulphonate crystallizing in needles, and the corresponding ortho salt crystallizing in plates or thin, lustrous scales. The latter is similar in appearance to the sodium parabromorthotoluenesulphonate described by Hübner and Post, and identical with the potassium salt prepared by Remsen and de Roode[1] by another method.

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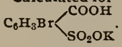
[1] Ann. Chem. (Liebig), 169, 1.

The potassium salt was then oxidized as follows: Into a 5-liter balloon flask containing about 4 liters of water, 90 grams of the salt, to be separately oxidized, were introduced. The flask was placed on an asbestos plate over a burner and connected with a boiler from which a current of steam was passed into the solution of the salt. After the solution had begun to boil, 100 grams of powdered potassium permanganate were added in small quantities at short intervals. The boiling was continued for twelve hours, when the oxidation was complete. During the operation the flame beneath the flask and the current of steam passing into the solution were so regulated that the quantity of water in the flask remained almost constant. When the salt was all oxidized, the excess of potassium permanganate was reduced with alcohol, the manganese dioxide allowed to settle, and the solution removed by decantation, and afterwards filtered. This was evaporated to a small volume and allowed to cool, when sufficient concentrated hydrochloric acid was added to precipitate the difficultly soluble acid potassium salt of parabromorthosulphobenzoic acid. This salt crystallizes from its aqueous solution in large, lustrous plates, and is identical with that prepared by Remsen and Bayley:[2]

	Calculated for  $C_6H_3Br<\begin{matrix}COOH\\SO_2OK\end{matrix}$.	Found.
K	12.22	12.15

Symmetrical Chloride.—The symmetrical chloride was prepared by the method employed for the preparation of the symmetrical chloride of orthosulphobenzoic acid. A mixture of powdered acid potassium salt of parabromorthosulphobenzoic acid and phosphorus pentachloride, in the proportion of 70 grams of the former to 114 grams of the latter, was placed in an evaporating dish on a water-bath and heated for an hour, the whole being frequently stirred during the heating.

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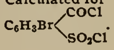
[1] This JOURNAL, **13**, 222.

[2] *Ibid.*, **8**, 230.

At the end of an hour the reaction was complete. The oily product was poured into a large beaker of cold water, where it soon solidified to a slightly yellowish, crystalline mass. This was powdered, washed with cold water, and dried. It was then treated with a cold solution of ammonia, made by adding 1 part of concentrated aqueous ammonia to 3 parts of water, until a portion crystallized from purified ligroin (boiling at 105° to 140°) showed a definite melting-point. The whole was then crystallized from the ligroin, which had been purified by the usual method. The symmetrical chloride melts at 99° to 100°.

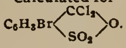
The determinations of chlorine in the chloride were made by the method employed by Saunders.[1] Portions of the chloride were decomposed in beakers by warming with concentrated nitric acid, to which silver nitrate had been added :

I. 0.1908 gram substance gave 0.1716 gram AgCl.[2]
II. 0.2369 gram substance gave 0.2124 gram AgCl.

	Calculated for  $C_6H_3Br\left\langle\begin{matrix}COCl\\SO_2Cl\end{matrix}\right.$.	Found.	
		I.	II.
Cl	22.30	22.24	22.17

Unsymmetrical Chloride.—The unsymmetrical chloride was prepared by the method devised by List and Stein[3] for the preparation of the unsymmetrical chloride of orthosulphobenzoic acid. The neutral potassium salt of parabromorthosulphobenzoic acid was heated with phosphorus oxychloride in a sealed tube at 130° for fifteen hours. For every 50 grams of the neutral salt, 75 grams of the phosphorus oxychloride were used. The yield was something over 50 per cent. When crystallized from ligroin, the unsymmetrical chloride melts at 89° to 90°.

I. 0.1542 gram substance gave 0.1393 gram AgCl.[4]
II. 0.2238 gram substance gave 0.2011 gram AgCl.

	Calculated for  $C_6H_3Br\left\langle\begin{matrix}CCl_2\\SO_2\end{matrix}\right\rangle O$.	Found.	
		I.	II.
Cl	22.30	22.34	22.22

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[1] This JOURNAL, 17, 350.

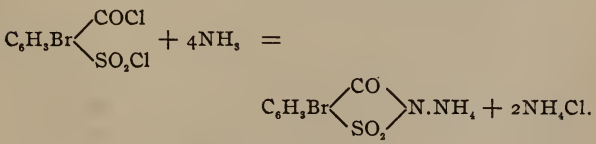
[2] Analysis made by E. S. Smith.

[3] *Loc. cit.*

[4] Analysis made by E. S. Smith.

Ammonia on the Symmetrical Chloride.—To 50 cc. concentrated, aqueous ammonia 5 grams finely powdered symmetrical chloride were added. The chloride was completely dissolved in about an hour. The solution was allowed to stand in the open air until the excess of ammonia had evaporated. The vessel was then found to contain a quantity of long, interlacing, needle-like crystals. When these were dissolved in water and sufficient hydrochloric acid added, a voluminous precipitate came down, which, when collected and crystallized from water, was found to be parabrombenzoic sulphinide, prepared first by Remsen and Bayley,[1] and later by Remsen and De Roode.[2] The filtrate from the parabrombenzoic sulphinide was evaporated to a smaller volume and examined for parabromorthocyanbenzenesulphonic acid. The addition of potassium carbonate gave no precipitate, and closer examination failed to reveal the presence of either the potassium or the ammonium salt of this acid.

This experiment was repeated a number of times, the conditions being varied, but always with the same result, whether the solution of ammonia was concentrated or dilute, cold or hot; the product was only parabrombenzoic sulphinide. It was found that the symmetrical chloride dissolves in cold, concentrated, aqueous ammonia in about an hour, while it is not completely dissolved in a solution made by mixing 1 part of concentrated ammonia with 1 part of water, before the end of four days. When the dilute ammonia is warmed, however, the chloride goes into solution in the course of a few hours:



$$C_6H_3Br\left\langle\begin{matrix}COCl\\SO_2Cl\end{matrix}\right. + 4NH_3 = C_6H_3Br\left\langle\begin{matrix}CO\\SO_2\end{matrix}\right\rangle N.NH_4 + 2NH_4Cl.$$

Ammonia on the Unsymmetrical Chloride.—To a concentrated solution of aqueous ammonia 5 grams of the unsymmetrical chloride were added. The chloride dissolved immediately, giving rise to a marked evolution of heat. After the excess of ammonia had evaporated, the solution was acidified with hydrochloric acid. The addition of the acid gave a white precipitate, which proved to be brombenzoic sulphinide, described above. The filtrate from the sulphinide was evaporated to a smaller volume, when the addition of potassium carbonate gave a precipitate of potassium parabromorthocyanbenzenesulphonate.[1]

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[1] This JOURNAL, 8, 229.

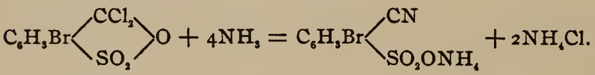
[2] *Ibid.*, 13, 230.

This experiment was repeated several times, under different conditions, and always with the same result. Both brombenzoic sulphinide and parabromorthocyanbenzenesulphonic acid were formed. Several experiments were performed in order to determine the relative amounts of the two products under different conditions. In each experiment 5 grams of the chloride were taken. The results are tabulated in grams.

	I.	II.	III.
1. In concentrated ammonia:			
Parabrombenzoic sulphinide	1.1	1.4	1.3
Potassium bromcyanbenzenesulphonate	3.6	3.4	3.3
2. In dilute ammonia (1 part conc. ammonia to 3 parts water):			
Parabrombenzoic sulphinide	0.7	0.6	0.6
Potassium bromcyanbenzenesulphonate	3.4	3.8	3.5
3. In very dilute ammonia (1 part conc. ammonia to 20 parts water):			
Parabrombenzoic sulphinide	0.28	0.26	0.31
Potassium bromcyanbenzenesulphonate	4.38	4.27	4.26

From the above table it will be seen that the more concentrated the ammonia the greater is the yield of the sulphinide.

The reaction by which the unsymmetrical chloride is converted into the ammonium salt of bromcyanbenzenesulphonic acid is expressed by the following equation:



$$C_6H_3Br\begin{matrix}\diagup CCl_2 \diagdown \\ \diagdown SO_2 \diagup\end{matrix}O + 4NH_3 = C_6H_3Br\begin{matrix}\diagup CN \\ \diagdown SO_2ONH_4\end{matrix} + 2NH_4Cl.$$

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[1] See page 504.

Whether another part of the unsymmetrical chloride is converted by the ammonia directly into the brombenzoic sulphinide, or is first changed into the symmetrical chloride, and then into the sulphinide, is not known.

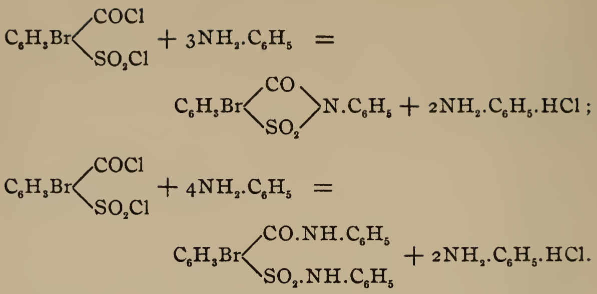
Aniline on the Symmetrical Chloride.—An emulsion of aniline and water was made by mixing 30 grams of aniline with 200 cc. of water in a large flask. To this mixture 25 grams of symmetrical chloride were slowly added. The chloride united at once with the aniline, forming a thick, yellowish, gummy substance, which, after being repeatedly shaken during twenty-four hours, had the appearance of a dark-brown powder. This was filtered off, washed first with cold, dilute hydrochloric acid, and then with water, and crystallized from alcohol. The product was placed on a perforated plate connected with a suction-pump, and slowly washed with a dilute solution of caustic soda until a portion of the filtrate collected in a test-tube no longer gave a precipitate when acidified with hydrochloric acid. The portion undissolved by the caustic soda was recrystallized from alcohol, from which it was obtained in long, slender needles, melting at 184° to 185°.

In accordance with the results obtained from a study of the chlorides of orthosulphobenzoic acid, this product must be regarded as the anil of parabromorthosulphobenzoic acid.

The filtrate containing the portion dissolved by the caustic soda, when acidified with hydrochloric acid, gave a white precipitate. This was collected and dissolved in boiling alcohol, from which it crystallized in short, silky needles. After being recrystallized several times, it showed a constant melting-point of 236° to 239°. This must be regarded as the symmetrical anilide of parabromorthosulphobenzoic acid.

The filtrate from the crude product obtained by the action of aniline on the symmetrical chloride was evaporated to a small volume, but yielded nothing but a small quantity of aniline hydrochloride.

The anil and the anilide are formed in about equal proportions :

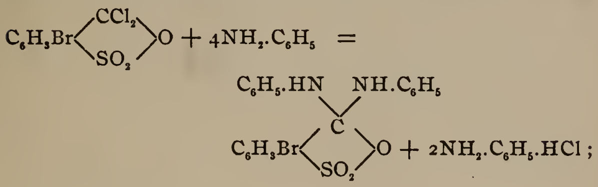


$$\mathrm{C_6H_3Br}\begin{matrix}\diagup \mathrm{COCl}\\ \diagdown \mathrm{SO_2Cl}\end{matrix} + \mathrm{3NH_2.C_6H_5} = \mathrm{C_6H_3Br}\begin{matrix}\diagup \mathrm{CO} \diagdown\\ \diagdown \mathrm{SO_2} \diagup\end{matrix}\mathrm{N.C_6H_5} + \mathrm{2NH_2.C_6H_5.HCl};$$

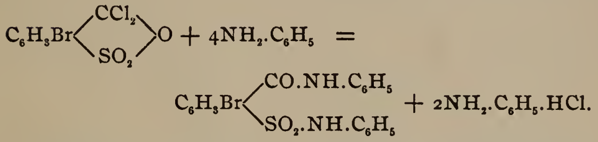
$$\mathrm{C_6H_3Br}\begin{matrix}\diagup \mathrm{COCl}\\ \diagdown \mathrm{SO_2Cl}\end{matrix} + \mathrm{4NH_2.C_6H_5} = \mathrm{C_6H_3Br}\begin{matrix}\diagup \mathrm{CO.NH.C_6H_5}\\ \diagdown \mathrm{SO_2.NH.C_6H_5}\end{matrix} + \mathrm{2NH_2.C_6H_5.HCl}.$$

Aniline on the Unsymmetrical Chloride.—An emulsion of aniline in water was made as in the preceding experiment. Thirty grams of aniline were mixed with 200 cc. of water in a large glask. To this mixture 25 grams of the unsymmetrical chloride were slowly added. In this case also, the chloride united at once with the aniline, but the reaction was a much cleaner one than in the case of the symmetrical chloride. In the course of a few hours, after repeated shaking, the flask was found to contain a white, homogeneous powder. This was collected and boiled with alcohol. About half of the product finally went into solution. From the alcoholic solution a quantity of fine, silky needles was obtained, which, when recrystallized several times, melted at 236° to 239°. This is identical with the symmetrical anilide obtained from the symmetrical chloride as described above. The first alcoholic solution and the first lot of crystals were examined carefully for the anil, but no trace of it was found.

The product undissolved by the alcohol was dissolved by a dilute solution of caustic soda, from which it was immediately precipitated by the addition of hydrochloric acid. It was again treated with hot alcohol to remove any trace of the symmetrical anilide that might be present, again dissolved by the caustic soda, and again precipitated. This operation was repeated until a pure, perfectly white, amorphous substance was obtained which did not fuse at 300°, though it showed some indications of decomposing slightly below that temperature. This must be regarded as the unsymmetrical anilide. The anilides are formed in about equal proportions :



$$C_6H_3Br\left\langle\begin{array}{l}CCl_2\\ SO_2\end{array}\right\rangle O + 4NH_2.C_6H_5 = C_6H_3Br\left\langle\begin{array}{c}\overset{C_6H_5.HN\quad NH.C_6H_5}{C}\\ SO_2\end{array}\right\rangle O + 2NH_2.C_6H_5.HCl\,;$$

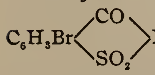


$$C_6H_3Br\left\langle\begin{array}{l}CCl_2\\ SO_2\end{array}\right\rangle O + 4NH_2.C_6H_5 = C_6H_3Br\left\langle\begin{array}{l}CO.NH.C_6H_5\\ SO_2.NH.C_6H_5\end{array}\right. + 2NH_2.C_6H_5.HCl.$$

Here, also, it is not known whether a part of the unsymmetrical chloride is converted directly into the symmetrical anilide, or passes first, under the influence of the aniline, into the symmetrical chloride, and is then converted into the symmetrical anilide.

The above experiments were repeated several times, under the same conditions, and always with the same results. It will thus be seen that when aniline acts upon the chlorides in the cold, the symmetrical anilide and the anil are formed from the symmetrical chloride, while the symmetrical and unsymmetrical anilides are formed from the unsymmetrical chloride ; in other words, the anil is obtained only from the symmetrical chloride, the unsymmetrical anilide only from the unsymmetrical chloride, while the symmetrical anilide is obtained from both. This was to be expected from the action of ammonia on the chlorides.

Anil of Parabromorthosulphobenzoic Acid,



$C_6H_3Br\left\langle\begin{array}{l}CO\\ SO_2\end{array}\right\rangle N.C_6H_5$.—As has been said, the anil is obtained only from the symmetrical chloride. It is only slightly soluble in cold but easily soluble in hot alcohol, and readily soluble in benzene, chloroform, acetone, and glacial acetic acid.

From its alcoholic solution it crystallizes at first in long, slender needles, sometimes 45 mm. in length, but when these are recrystallized several times they assume the form of long, narrow, very thin plates. The anil melts at 184°.5.

0.2475 gram substance gave 0.1759 gram $BaSO_4$.

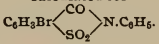
0.2451 gram substance gave 0.1696 gram $BaSO_4$.

0.2141 gram substance gave 0.00893 gram N.

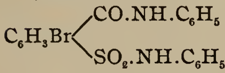
0.2675 gram substance gave 0.01104 gram N.

0.1843 gram substance gave 0.3122 gram CO_2 and 0.0400 gram H_2O.

0.2141 gram substance gave 0.3601 gram CO_2 and 0.0514 gram H_2O.

	Calculated for	Found.	
	 $C_6H_3Br\left\langle\begin{matrix}CO\\SO_2\end{matrix}\right\rangle N.C_6H_5$.	I.	II.
C	46.15	46.20	45.87
H	2.36	2.41	2.66
S	9.46	9.50	9.39
N	4.14	4.17	4.12

Symmetrical Anilide of Parabromorthosulphobenzoic Acid,


$C_6H_3Br\left\langle\begin{matrix}CO.NH.C_6H_5\\SO_2.NH.C_6H_5\end{matrix}\right.$.—This substance is obtained both from the symmetrical and the unsymmetrical chloride. It is not soluble to any extent even in boiling alcohol, but is readily soluble in chloroform, acetone, benzene, and glacial acetic acid. It crystallizes in fine, silky needles. If the anilide in crystalline form is finely powdered and treated with a dilute solution of caustic soda, it goes into solution very slowly, nor will it be completely dissolved, however long it stands in contact with the alkali. The solution of the caustic soda, with whatever amount of the anilide it has dissolved, must be removed and a fresh portion of the alkali added, and this operation repeated a number of times, before the anilide is completely dissolved. Hydrochloric acid precipitates the anilide in amorphous form from its solution in caustic soda. The amorphous anilide is readily dissolved by the caustic soda. The symmetrical anilide melts at 236° to 239°, but if heated

rapidly to 238°, and if the source of heat is then removed, it will melt at 238° to 239°.

0.2357 gram substance gave 0.1343 gram $BaSO_4$.

0.1915 gram substance gave 0.1090 gram $BaSO_4$.

0.2949 gram substance gave 0.01922 gram N.

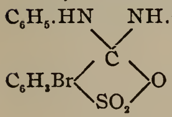
0.3176 gram substance gave 0.0207 gram N.

0.1919 gram substance gave 0.3699 gram CO_2 and 0.0631 gram H_2O.

0.2208 gram substance gave 0.4244 gram CO_2 and 0.0729 gram H_2O.

	Calculated for $C_6H_3Ba\left\langle\begin{array}{l}CO.NH.C_6H_5\\SO_2.NH.C_6H_5\end{array}\right.$.	Found.	
		I.	II.
C	52.90	52.52	52.42
H	3.50	3.65	3.67
S	7.42	7.78	7.79
N	6.49	6.50	6.52

Unsymmetrical Anilide of Parabromorthosulphobenzoic Acid,

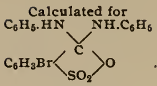


.—The unsymmetrical anilide is obtained only from the unsymmetrical chloride. It differs markedly from the symmetrical aniline in its behavior towards solvents. It is readily dissolved by a dilute solution of caustic soda, but is only slightly soluble in those other solvents in which the symmetrical anilide is easily dissolved. When it is boiled with absolute alcohol or with glacial acetic acid, it is dissolved to a slight extent, and if the solution is allowed to stand for several days the unsymmetrical anilide crystallizes out in fine, very short needles, which, like the amorphous form, do not fuse at 300°. Unlike the crystalline form of the symmetrical anilide, the crystals of the unsymmetrical anilide are dissolved at once upon the addition of dilute caustic soda.

0.1958 gram substance gave 0.1112 gram $BaSO_4$.

0.3118 gram substance gave 0.01675 gram N.

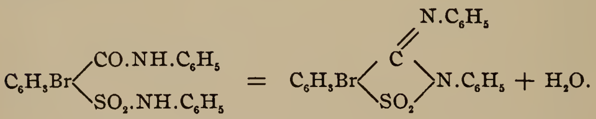
0.2085 gram substance gave 0.4040 gram CO_2 and 0.0690 gram H_2O.

	Calculated for  $C_6H_3Br\left\langle\begin{array}{c}\overset{C_6H_5.HN\ \ NH.C_6H_5}{C}\\SO_2\end{array}\right\rangle O$	Found.
C	52.90	52.84
H	3.50	3.73
S	7.42	7.79
N	6.49	6.55

Action of Dehydrating Agents on the Symmetrical Anilide.

a. Phosphorus Pentoxide.—A mixture of the anilide and phosphorus pentoxide in the proportion of about 2 parts of the one to 5 parts of the other, was placed in a large test-tube closed with a cork stopper carrying a Bunsen valve, and heated to 180° for two hours. The anilide was partially transformed into a yellowish-brown substance, which dissolved readily in hot alcohol or glacial acetic acid. From these solvents it crystallized in dark-brown needles, melting at 200°.

In accordance with the work of Remsen and Hunter[1] on the anilides of orthosulphobenzoic acid, this must be regarded as the dianil of parabromorthosulphobenzoic acid formed from the anilide by elimination of the constituents of 1 molecule of water :



$$C_6H_3Br\left\langle\begin{array}{l}CO.NH.C_6H_5\\SO_2.NH.C_6H_5\end{array}\right. = C_6H_3Br\left\langle\begin{array}{c}\overset{N.C_6H_5}{\overset{/\!/}{C}}\\SO_2\end{array}\right\rangle N.C_6H_5 + H_2O.$$

b. Phosphorus Oxychloride.—The symmetrical anilide was placed in a tubulated retort connected with a return condenser, and about ten times its weight of phosphorus oxychloride added. Sufficient heat was applied to bring the phosphorus oxychloride to gentle boiling. As soon as the liquid began to boil, a yellowish color made its appearance, and at the end of an hour all the anilide had reacted with the dehydrating agent, giving rise to a clear, dark-brown solution. The excess of phosphorus oxychloride was distilled off under diminished pressure, when a yellowish mass remained in the retort. This was washed with water, dried, and crystallized several times from glacial acetic acid, when it was finally obtained in the form of small, bright-yellow plates, melting at 199° to 200°. This is the dianil, identical with the product obtained by the action of phosphorus pentoxide on the symmetrical anilide.

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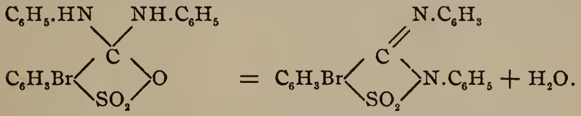
[1] This Journal, **18**, 809.

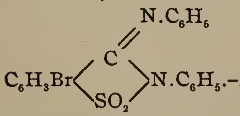
Action of Dehydrating Agents on the Unsymmetrical Anilide.

a. Phosphorus Pentoxide.—A mixture of equal parts of the unsymmetrical anilide and phosphorus pentoxide was heated to 180° in a closed test-tube for five hours. The same change was observed and the same product formed as in the case of the symmetrical anilide, but longer heating was required than was necessary with the latter.



b. Phosphorus Oxychloride.—The unsymmetrical anilide was boiled with phosphorus oxychloride in a tubulated retort connected with a return condenser. At the end of an hour, the anilide had completely dissolved, giving rise to a dark-brown solution. The excess of phosphorus oxychloride was distilled off under diminished pressure and the yellow residue crystallized from glacial acetic acid. Small, yellow crystals were obtained identical with the product from the reaction of phosphorus oxychloride on the symmetrical chloride.

Dianil of Parabromorthosulphobenzoic Acid,



.–As has just been stated, this substance can be prepared from both the symmetrical and the unsymmetrical anilide by the action of phosphorus pentoxide or of phosphorus oxychloride. It is obtained the more easily by the latter method. It must be regarded as formed by the abstraction of the constituents of 1 molecule of water from each molecule of the anilide. It is a beautiful, yellow compound, crystallizing from glacial acetic acid in small plates melting at

119° to 200°. It is readily soluble in alcohol, benzene, and chloroform. If a solution of the dianil in glacial acetic acid or in alcoholic potash is boiled for some time, it takes up one molecule of water and passes into the unsymmetrical anilide.

0.3836 gram substance gave 0.2169 gram $BaSO_4$.

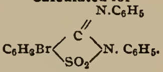
0.3195 gram substance gave 0.1831 gram $BaSO_4$.

0.2693 gram substance gave 0.0184 gram N.

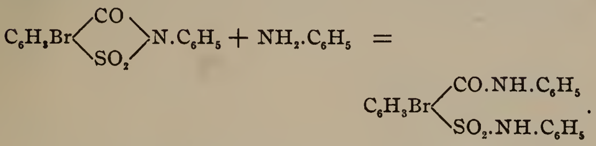
0.2643 gram substance gave 0.01786 gram N.

0.2141 gram substance gave 0.4324 gram CO_2 and 0.0646 gram H_2O.

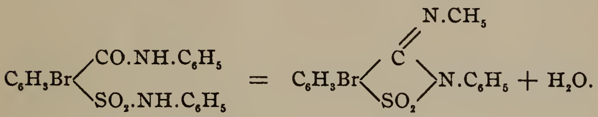
0.2149 gram substance gave 0.4337 gram CO_2 and 0.0651 gram H_2O.

	Calculated for 	Found.	
		I.	II.
C	55.20	55.08	55.04
H	3.14	3.35	3.36
N	6.77	6.73	6.75
S	7.74	7.85	7.85

Transformation of the Anil into the Symmetrical Anilide.—Two grams of the anil were placed in a tubulated retort connected with a return condenser, and about ten times its weight of aniline added. Sufficient heat was applied to bring the aniline to gentle boiling. In an hour and a half the anil was completely dissolved, the solution being much darker than the original aniline. The solution was cooled and diluted with twenty times its volume of water, and the excess of aniline neutralized with hydrochloric acid. Upon the addition of the acid, a dark-brown product was precipitated. This was collected on a filter connected with a suction-pump, washed well with cold water, and then with a dilute solution of caustic soda as long as it continued to be dissolved by the alkali. In time it was almost completely dissolved, only a dark-brown, almost black, residue, being left on the filter. The alkaline filtrate was acidified with hydrochloric acid, and the white precipitate formed dissolved in hot alcohol. The product crystallized from the alcoholic solution in short, silky needles melting at 235° to 239°. This proved it to be the symmetrical anilide:

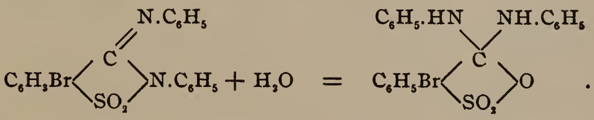


Transformation of the Symmetrical Anilide into the Dianil.—As has been described above, this transformation can easily be effected by heating the anilide with phosphorus pentoxide, or by boiling it with phosphorus oxychloride:

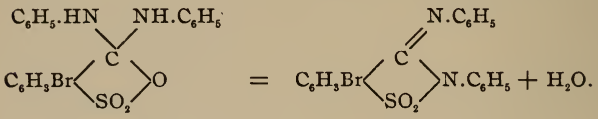


Transformation of the Dianil into the Unsymmetrical Anilide.—This can be accomplished by boiling a solution of the dianil in glacial acetic acid or in alcoholic potash. Into a 300 cc. round flask there were introduced 100 grams of alcohol, 2 grams of caustic potash, and 2 grams of the dianil. The flask was connected with a return condenser and the solution boiled for two hours. Most of the alcohol was then distilled off and the remaining solution diluted with water. The solution was acidified with hydrochloric acid. The precipitate, which was immediately formed, proved to be the unsymmetrical anilide.

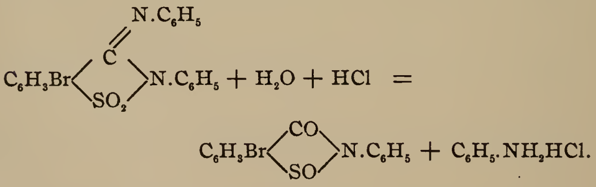
A small quantity of the dianil was dissolved in hot glacial acetic acid and the solution boiled for half an hour. After the solution had cooled, the unsymmetrical anilide crystallized out in very short needles along with some of the unchanged dianil:



Transformation of the Unsymmetrical Anilide into the Dianil.—As has already been described, this transformation is easily effected by heating the unsymmetrical anilide with phosphorus pentoxide or by boiling it with phosphorus oxychloride :



Transformation of the Dianil into the Anil.—Two grams of finely powdered dianil were placed in a tubulated retort connected with a return condenser, and about 100 grams of concentrated hydrochloric acid added. The acid was then boiled. As soon as the boiling began, the yellow color of the dianil began to grow fainter, and in an hour and a half it had completely disappeared. The undissolved contents of the retort were transferred to a beaker, diluted with water, filtered, and washed free from hydrochloric acid. The product was dissolved in alcohol, from which it crystallized in needles melting at 184° to 185°. This proved to be the anil of parabromorthosulphobenzoic acid :



It will be readily seen that the above transformations are identical with those described by Remsen and Hunter[1] in the case of the corresponding compounds from orthosulphobenzoic acid. They may be graphically represented by the following diagram :

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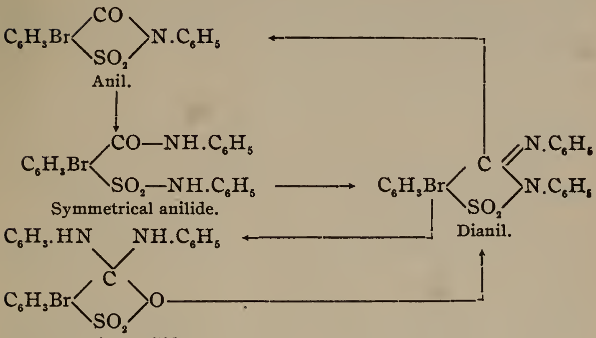
[1] *Loc. cit.*



The above transformations suggested the possibility of passing directly from one chloride to the other. Since in the preparation of the unsymmetrical chloride none of the symmetrical compound is every found, it seemed possible that this chloride might be transformed into the other by heating with phosphorus oxychloride.

Five grams of the symmetrical chloride were heated with several times its weight of phosphorus oxychloride in a sealed tube at 130° for five hours. The phosphorus oxychloride was then distilled off under diminished pressure and the residue crystallized from ligroin. The crystals melted at the same temperature as before heating, showing that no change had taken place.

Portions of each chloride were next heated in sealed tubes in a sulphuric acid-bath at 106° for three days. As long as the temperature remained above 100°, both chlorides remained in the liquid state. At the end of three days the tubes were opened. In each there was noticed the odor of hydrochloric acid. Upon the walls of each tube was found a small quantity of a sublimate which had collectly mostly in the form of fine needles. That from the symmetrical compound melted at 99°, the melting-point of the symmetrical chloride, that from the unsymmetrical compound, melted at 89°, the melting-point of the unsymmetrical chloride. The products in the tubes were then crystallized from ligroin, and one was found to be the unchanged symmetrical chloride, and the other the unchanged unsymmetrical chloride.

Summary.

By the experiments recorded above, the following facts are established :

1. With the higher melting chloride, ammonia gives only one product, parabrombenzoic sulphinide.
2. With the lower melting chloride, ammonia gives two products, parabrombenzoic sulphinide and ammonium parabromorthocyanbenzenesulphonate, the proportion of the former decreasing with the dilution of the ammonia, being 26 per cent with concentrated ammonia, 15 per cent with dilute ammonia (1 to 3), and 6 per cent with very dilute ammonia (1 to 20).
3. Aniline in the cold gives with the higher melting chloride two products, the anil and the fusible anilide.
4. Aniline in the cold gives with the lower melting chloride two products, the fusible and infusible anilides.
5. Dehydrating agents convert the anilides into a dianil, and only one dianil is known.
6. Passage can readily be effected from the anil on the one side to the infusible aniline on the other by passing through the fusible anilide and the dianil. On the other hand, the infusible anilide can readily be converted into the anil through the dianil.
7. The higher melting chloride is unchanged when heated in a sealed tube with phosphorus oxychloride at 130°, and neither chloride is appreciably decomposed when kept in the liquid state in a sealed tube for several days.

These results are in accordance with those published by Professor Remsen and some of his students in this JOURNAL upon the chlorides of orthosulphobenzoic acid, to which references have already been made, and are not in accordance with the statements of List and Stein,[1] to which reference has also been made. It seems that these chlorides are isomeric and not tautomeric substances, that they are separate and distinct from each other, and that each is as much entitled to its individual constitutional formula as any other stable chemical compound is. Evidence points to the symmetrical structure for the higher melting chloride, and to the unsymmetrical structure for the lower melting chloride. These compounds should, therefore, be represented thus :

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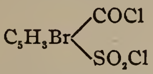
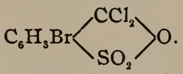
[1] *Loc. cit.*



$$C_5H_3Br\left\langle\begin{matrix}COCl\\SO_2Cl\end{matrix}\right.$$

Symmetrical chloride.

and

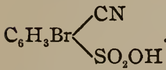


$$C_6H_3Br\left\langle\begin{matrix}CCl_2\\SO_2\end{matrix}\right\rangle O.$$

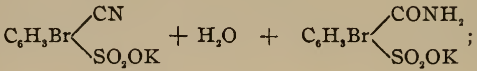
Unsymmetrical chloride.

PART II.

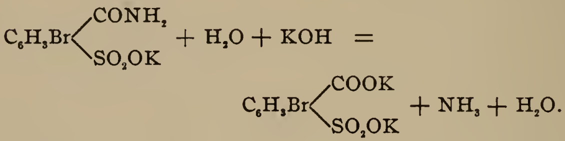
The remainder of this article will be devoted to a description of the properties and some of the derivatives of three acids obtained either directly or indirectly from the chlorides. Of these acids, parabromorthocyanbenzenesulphonic acid and parabromorthocarbaminesulphonic acid come from the unsymmetrical chloride, and parabromorthosulphaminebenzoic acid comes from the symmetrical chloride. The results of a further study of parabrombenzoic sulphinide will also be included here.



Parabromorthocyanbenzenesulphonic Acid, $C_6H_3Br\left\langle\begin{matrix}CN\\SO_2OH\end{matrix}\right.$.—As has been said, when the unsymmetrical chloride is dissolved in ammonia, the main product of the reaction is the ammonium salt of parabromorthocyanbenzenesulphonic acid. This can readily be converted into the barium salt, from which the free acid can be obtained by precipitating the barium. It can also be prepared by boiling with water parabromorthocyansulphone chloride, which is one of the products of the action of phosphorus pentachloride upon parabrombenzoic sulphinide. The acid is very soluble in water. When an aqueous solution of the acid is boiled for five hours with dilute hydrochloric acid it remains unchanged; when, however, its alkali salts are boiled for five hours with dilute sodium hydroxide or potassium hydroxide they are converted into the sodium or the potassium salt of parabromorthocarbaminesulphonic acid, and, if the boiling is continued ten hours longer, they are partially converted into the corresponding salts of parabromorthosulphobenzoic acid. The changes are represented as follows :

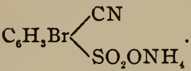
1. 

$$C_6H_3Br<^{CN}_{SO_2OK} + H_2O + C_6H_3Br<^{CONH_2}_{SO_2OK};$$

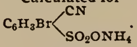
2. 

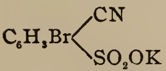
$$C_6H_3Br<^{CONH_2}_{SO_2OK} + H_2O + KOH = C_6H_3Br<^{COOK}_{SO_2OK} + NH_3 + H_2O.$$

The other salts of the acid are easily prepared by starting with the ammonium salt.

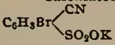
Ammonium Parabromorthocyanbenzenesulphonate,  $C_6H_3Br<^{CN}_{SO_2ONH_4}$.—This salt was obtained by dissolving the unsymmetrical chloride in ammonia. It is very soluble in water, much less soluble in alcohol. From its aqueous solution it crystallizes in small, lustrous plates, which have an extremely bitter taste.

0.3630 gram substance gave 0.2183 gram NH_3.
0.3081 gram substance gave 0.1847 gram NH_3.

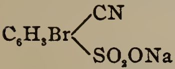
	Calculated for	Found.	
	 $C_6H_3Br<^{CN}_{SO_2ONH_4}$.	I.	II.
NH_3	6.09	6.01	6.00

Potassium Parabromorthocyanbenzenesulphonate,  $C_6H_3Br<^{CN}_{SO_2OK} + 1\frac{1}{2}H_2O$.—The potassium salt was made by adding a solution of potassium carbonate or potassium hydroxide to a solution of the ammonium salt. The potassium salt, being much less soluble than the ammonium salt, is precipitated. It is readily soluble in hot water, but much less soluble in cold. From its aqueous solution it crystallizes in fine, silky needles having a bitter taste.

0.1947 gram substance lost 0.0160 gram H_2O.
0.1909 gram substance lost 0.0158 gram H_2O.
0.1947 gram substance gave 0.0513 gram K_2SO_4.
0.1909 gram substance gave 0.0504 gram K_2SO_4.

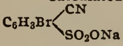
	Calculated for  $C_6H_3Br\Big\langle\begin{matrix}CN\\SO_2OK\end{matrix} + 1\frac{1}{2}H_2O$.	Found. I.	 II.
H_2O	8.25	8.22	8.27
K	11.92	11.80	11.83

Sodium Parabromorthocyanbenzenesulphonate,

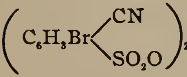


$C_6H_3Br\Big\langle\begin{matrix}CN\\SO_2ONa\end{matrix} + 1\frac{1}{2}H_2O$.—The sodium salt was made by adding a solution of sodium carbonate or sodium hydroxide to a fairly concentrated solution of the ammonium salt. It is much more soluble in hot than in cold water, and crystallizes in long, silky needles, resembling the potassium salt.

0.2379 gram substance lost 0.0209 gram H_2O.
0.2178 gram substance lost 0.0189 gram H_2O.
0.2379 gram substance gave 0.0530 gram Na_2SO_4.
0.2178 gram substance gave 0.0492 gram Na_2SO_4.

	Calculated for  $C_6H_3Br\Big\langle\begin{matrix}CN\\SO_2ONa\end{matrix} + 1\frac{1}{2}H_2O$.	Found. I.	 II.
H_2O	8.68	8.76	8.72
Na	7.39	7.21	7.31

Barium Parabromorthocyanbenzenesulphonate,



$\left(C_6H_3Br\Big\langle\begin{matrix}CN\\SO_2O\end{matrix}\right)_2Ba + 6H_2O$.—The barium salt was prepared by adding a warm, saturated solution of barium hydroxide to a hot, concentrated solution of the ammonium salt. When the mixture cooled, the barium salt, mixed with some of the ammonium salt, crystallized out of the solution in long needles. After several crystallizations it was obtained quite pure in long, lustrous, rectangular plates.

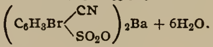
It can also be prepared by neutralizing the free acid with barium carbonate. In this way it was once obtained crystallizing in prisms with 3 molecules of water, as will be described later.

If a solution of barium hydroxide is added to a dilute solution of the ammonium salt, and an attempt is made to obtain the barium salt by evaporating the solution, a basic salt will be precipitated. This is very difficultly soluble in cold or hot water, and contains between 36 and 37 per cent of barium.

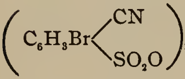
0.3166 gram substance gave 0.1947 gram $BaSO_4$.

An analysis of the pure barium salt gave the following results :

0.2803 gram substance lost 0.0396 gram H_2O.
0.2554 gram substance lost 0.0359 gram H_2O.
0.2803 gram substance gave 0.0855 gram $BaSO_4$.
0.2554 gram substance gave 0.0779 gram $BaSO_4$.

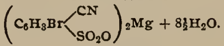
	Calculated for  $\left(C_6H_3Br\begin{matrix}CN\\SO_2O\end{matrix}\right)_2Ba + 6H_2O$.	Found. I.	 II.
H_2O	14.08	14.13	14.05
Ba	17.86	17.94	17.90

Magnesium Parabromorthocyanbenzenesulphonate,



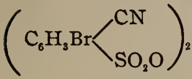
$\left(C_6H_3Br\begin{matrix}CN\\SO_2O\end{matrix}\right)_2Mg + 8\frac{1}{2}H_2O$.—The magnesium salt was made by adding to a solution of the barium salt just enough magnesium sulphate to precipitate all the barium. It is readily soluble in hot water, much less soluble in cold, and from its aqueous solution crystallizes in diamond-shaped tables, the crystals often having a hopper appearance.

0.2258 gram substance lost 0.0493 gram H_2O.
0.2267 gram substance lost 0.0492 gram H_2O.
0.2073 gram substance lost 0.0448 gram H_2O.
0.2258 gram substance gave 0.0374 gram $MgSO_4$.
0.2267 gram subsrance gave 0.0382 gram $MgSO_4$.
0.2073 gram substance gave 0.0349 gram $MgSO_4$.

	Calculated for  $\left(C_6H_3Br\begin{matrix}CN\\SO_2O\end{matrix}\right)_2Mg + 8\frac{1}{2}H_2O$.	 I.	Found. II.	 III.
H_2O	21.88	21.88	21.71	21.61
Mg	3.43	3.31	3.37	3.36

The zinc salt was also prepared. It crystallizes in small plates, and, like the magnesium salt, contains 8.5 molecules of water of crystallization.

Copper Parabromorthocyanbenzenesulphonate,

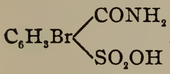


$\left(C_6H_3Br\begin{matrix}CN\\SO_2O\end{matrix}\right)_2Cu + 4H_2O$.—The copper salt was made from the barium salt by precipitating the barium with pure copper sulphate. It crystallizes in fine needles or long, thin plates of a delicate blue color. It is very soluble in water.

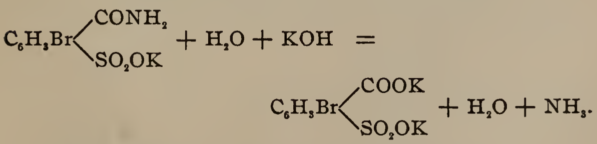
0.2230 gram substance lost 0.0242 gram H_2O.
0.2046 gram substance lost 0.0221 gram H_2O.
0.2046 gram substance gave 0.0233 gram CuO.

	Calculated for $\left(C_6H_3Br\begin{matrix}CN\\SO_2O\end{matrix}\right)_2Cu + 4H_2O$.	Found. I.	Found. II.
H_2O	10.90	10.85	10.81
Cu	9.58	....	9.22

Parabromorthocarbaminebenzenesulphonic Acid,

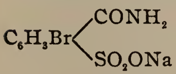


$C_6H_3Br\begin{matrix}CONH_2\\SO_2OH\end{matrix}$.—The free acid was not obtained and only the sodium and potassium salts were prepared. When these are boiled for ten hours with dilute sodium hydroxide or potassium hydroxide they are partly converted into the corresponding salts of parabromorthosulphobenzoic acid :



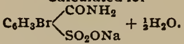
$$C_6H_3Br\begin{matrix}CONH_2\\SO_2OK\end{matrix} + H_2O + KOH = C_6H_3Br\begin{matrix}COOK\\SO_2OK\end{matrix} + H_2O + NH_3.$$

Sodium Parabromorthocarbaminebenzenesulphonate,

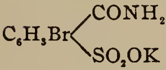


$C_6H_3Br\begin{matrix}CONH_2\\SO_2ONa\end{matrix} + \frac{1}{2}H_2O$.—This salt was prepared by boiling for five hours a solution of ammonium or sodium parabromorthocyanbenzenesulphonate with dilute sodium hydroxide. The solution was filtered, evaporated to a small volume, and allowed to stand for several days over sulphuric acid, when the sodium parabromorthocarbaminesulphonate crystallized out in short needles in wart-like clusters. The salt is very soluble in water.

0.2041 gram substance lost 0.0066 gram H_2O.
0.1919 gram substance lost 0.0055 gram H_2O.
0.2041 gram substance gave 0.0462 gram Na_2SO_4.
0.1919 gram substance gave 0.0439 gram Na_2SO_4.

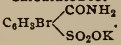
	Calculated for	Found.	
	 $C_6H_3Br\Big\langle\begin{matrix}CONH_2\\ SO_2ONa\end{matrix} + \frac{1}{2}H_2O.$	I.	II.
H_2O	3.07	2.93	2.86
Na	7.40	7.33	7.41

Potassium Parabromorthocarbaminebenzenesulphonate,

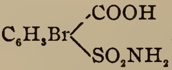

$C_6H_3Br\Big\langle\begin{matrix}CONH_2\\ SO_2OK\end{matrix}$

.—The potassium salt was made by boiling for five hours a solution of ammonium or potassium parabromorthocyanbenzenesulphonate with dilute potassium hydroxide. The solution was filtered, evaporated to a small volume, and allowed to stand for several days, when the potassium parabromorthocarbaminesulphonate crystallized out in short needles, radiating from a common center.

0.1746 gram substance gave 0.0479 gram K_2SO_4.
0.2011 gram substance gave 0.0552 gram K_2SO_4.
0.1729 gram substance gave 0.0471 gram K_2SO_4.

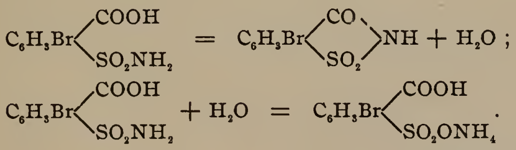
	Calculated for		Found.	
	 $C_6H_3Br\Big\langle\begin{matrix}CONH_2\\ SO_2OK\end{matrix}.$	I.	II.	III.
K	12.26	12.36	12.33	12.24

Parabromorthosulphaminebenzoic Acid,


$C_6H_3Br\Big\langle\begin{matrix}COOH\\ SO_2NH_2\end{matrix}$

.—This acid is easily prepared by hydrolyzing parabrombenzoic sulphinide. Fifteen grams of the sulphinide were placed in a liter balloon flask containing 0.5 liter of water and attached to a return condenser. A little more potassium hydroxide was added than was necessary to neutralize the sulphinide.

Heat was applied and the solution kept gently boiling for five hours. It was then filtered off, and after it had cooled enough hydrochloric acid was added to precipitate all the sulphamine acid. The acid crystallizes in long, very thin, lustrous plates. It is readily soluble in hot water, but only slightly soluble in cold. It has no sharp melting-point, but after being recrystallized several times it melts constantly at 192° to 197°. When heated to 127° in a covered crucible, it begins to lose water of constitution and pass over partly into parabrombenzoic sulphinide, which collects in the top of the crucible; but this water unites with another portion of the sulphamine acid, converting it into the acid ammonium salt of parabromorthosulphobenzoic acid, which does not sublime, but remains in the base of the crucible. A portion of the sulphamine acid was heated for thirty hours at 160°. It was weighed from time to time and found to be diminishing in weight at the rate of about a milligram every three hours. At the end of the thirty hours only a small quantity of the sulphinide had collected in the top of the crucible. The product in the base of the crucible was comparatively pure acid ammonium parabromorthosulphobenzoate. Hence the loss in weight was due largely to the subliming of the sulphinide out of the crucible. The changes here described are represented as follows:

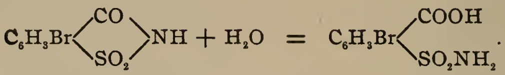


$$\mathrm{C_6H_3Br}\left\langle\begin{array}{l}\mathrm{COOH}\\ \mathrm{SO_2NH_2}\end{array}\right. = \mathrm{C_6H_3Br}\left\langle\begin{array}{l}\mathrm{CO}\\ \mathrm{SO_2}\end{array}\right\rangle\mathrm{NH} + \mathrm{H_2O};$$

$$\mathrm{C_6H_3Br}\left\langle\begin{array}{l}\mathrm{COOH}\\ \mathrm{SO_2NH_2}\end{array}\right. + \mathrm{H_2O} = \mathrm{C_6H_3Br}\left\langle\begin{array}{l}\mathrm{COOH}\\ \mathrm{SO_2ONH_4}\end{array}\right. .$$

When the free sulphamine acid is boiled with dilute hydrochloric acid, it passes rapidly over into the acid ammonium salt of parabromorthosulphobenzoic acid, but if the alkali salts of the acid are boiled with dilute alkalies this hydrolysis does not take place even when the heating is continued for ten hours.

Parabromorthosulphaminebenzoic acid can be prepared also by boiling parabrombenzoic sulphinide with dilute hydrochloric acid, provided the heating is not continued longer than forty-five minutes :



$$C_6H_3Br\left\langle\begin{matrix}CO\\SO_2\end{matrix}\right\rangle NH + H_2O = C_6H_3Br\left\langle\begin{matrix}COOH\\SO_2NH_2\end{matrix}\right. .$$

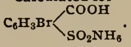
If the boiling is carried on for a longer time, the product is the acid ammonium salt of parabromorthosulphobenzoic acid.

The salts of the sulphamine acid are more soluble in water than the free acid. They are prepared in the usual way. When heated above 150°, they pass over into the corresponding salts of parabrombenzoic sulphinide.

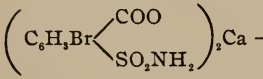
The alkali salts are very soluble. The strontium, barium, magnesium, and calcium salts, in their solubility, follow each other in the order named, the calcium salt being but slightly soluble in water.

An analysis of the free acid gave the following results :

0.2439 gram substance gave 0.2026 gram $BaSO_4$.
0.2195 gram substance gave 0.01103 gram N.
0.2427 gram substance gave 0.01129 gram N.

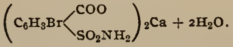
	Calculated for	Found.		
	 $C_6H_3Br\left\langle\begin{matrix}COOH\\SO_2NH_6\end{matrix}\right.$.	I.	II.	III.
S	11.42	11.38	....	....
N	5.00	....	5.02	5.06

Calcium Parabromorthosulphaminebenzoate,

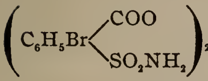


$\left(C_6H_3Br\left\langle\begin{matrix}COO\\SO_2NH_2\end{matrix}\right.\right)_2Ca + 2H_2O$.—The calcium salt crystallizes slowly from its aqueous solution in large prisms having hemihedral faces.

0.2381 gram substance lost 0.0135 gram H_2O.
0.2737 gram substance lost 0.0127 gram H_2O.
0.2381 gram substance gave 0.0513 gram $CaSO_4$.
0.2237 gram substance gave 0.0482 gram $CaSO_4$.

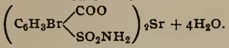
	Calculated for	Found.	
	 $\left(C_6H_3Br\left\langle\begin{matrix}COO\\SO_2NH_2\end{matrix}\right.\right)_2Ca + 2H_2O$.	I.	II.
H_2O	5.67	5.67	5.67
Ca	6.41	6.33	6.33

Strontium Parabromorthosulphaminebenzoate,

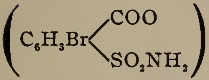


$\left(C_6H_5Br{<}\begin{matrix}COO\\SO_2NH_2\end{matrix}\right)_2Sr + 4H_2O$.—The strontium salt is much more soluble than the calcium salt. From its aqueous solution it crystallizes in long, slender needles.

0.2048 gram substance lost 0.0210 gram H_2O.
0.2237 gram substance lost 0.0230 gram H_2O.
0.2048 gram substance gave 0.0529 gram $SrSO_4$.
0.2237 gram substance gave 0.0570 gram $SrSO_4$.

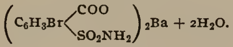
	Calculated for  $\left(C_6H_3Br{<}\begin{matrix}COO\\SO_2NH_2\end{matrix}\right)_2Sr + 4H_2O$.	Found. I.	II.
H_2O	10.04	10.25	10.28
Sr	12.17	12.30	12.13

Barium Parabromorthosulphaminebenzoate,

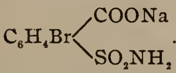


$\left(C_6H_3Br{<}\begin{matrix}COO\\SO_2NH_2\end{matrix}\right)_2Ba + 2H_2O$.—The barium salt is readily soluble in hot water, much less soluble in cold. From its aqueous solution it crystallizes in short needles.

0.2583 gram substance lost 0.0124 gram H_2O.
0.2157 gram substance lost 0.0104 gram H_2O.
0.2234 gram substance gave 0.0716 gram $BaSO_4$.
0.2157 gram substance gave 0.0685 gram $BaSO_4$.

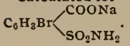
	Calculated for  $\left(C_6H_3Br{<}\begin{matrix}COO\\SO_2NH_2\end{matrix}\right)_2Ba + 2H_2O$.	Found. I.	II.
H_2O	4.92	4.80	4.82
Ba	18.73	18.85	18.67

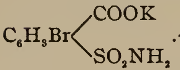
Sodium Parabromorthosulphaminebenzoate,



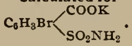
$C_6H_4Br{<}\begin{matrix}COONa\\SO_2NH_2\end{matrix}$.—The sodium salt is very soluble in water. After standing over sulphuric acid it crystallizes in short needles from the concentrated solution.

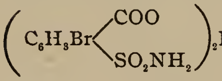
0.2084 gram substance gave 0.0493 gram Na_2SO_4.
0.2582 gram substance gave 0.0612 gram Na_2SO_4.

	Calculated for  $\mathrm{C_6H_3Br}\begin{smallmatrix}\mathrm{COONa}\\ \mathrm{SO_2NH_2}\end{smallmatrix}$.	Found. I.	II.
Na	7.61	7.66	7.67

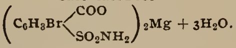
Potassium Parabromorthosulphaminebenzoate,  $\mathrm{C_6H_3Br}\begin{smallmatrix}\mathrm{COOK}\\ \mathrm{SO_2NH_2}\end{smallmatrix}$.—The potassium salt is very soluble even in cold water, but not so soluble as the sodium salt. On standing over sulphuric acid, it crystallizes from a concentrated solution in large, rectangular plates, often arranged in clusters.

0.2015 gram substance gave 0.0553 gram K_2SO_4.
0.2365 gram substance gave 0.0650 gram K_2SO_4.

	Calculated for  $\mathrm{C_6H_3Br}\begin{smallmatrix}\mathrm{COOK}\\ \mathrm{SO_2NH_2}\end{smallmatrix}$.	Found. I.	II.
K	12.26	12.29	12.31

Magnesium Parabromorthosuphaminebenzoate,  $\left(\mathrm{C_6H_3Br}\begin{smallmatrix}\mathrm{COO}\\ \mathrm{SO_2NH_2}\end{smallmatrix}\right)_2\mathrm{Mg} + 3H_2O$.—The magnesium salt was prepared from the barium salt by adding magnesium sulphate to precipitate all the barium. It crystallizes in short needles arranged in tufts.

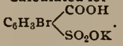
0.2807 gram substance lost 0.0241 gram H_2O.
0.2099 gram substance lost 0.0180 gram H_2O.
0.2476 gram substance gave 0.0454 gram $MgSO_4$.
0.2807 gram substance gave 0.0511 gram $MgSO_4$.
0.2099 gram substance gave 0.0390 gram $MgSO_4$.

	Calculated for  $\left(\mathrm{C_6H_3Br}\begin{smallmatrix}\mathrm{COO}\\ \mathrm{SO_2NH_2}\end{smallmatrix}\right)_2\mathrm{Mg} + 3H_2O$.	Found. I.	II.	III.
H_2O	8.49	8.58	8.57	....
Mg	3.77	3.66	3.64	3.71

The copper salt was also prepared. It is insoluble in water and is precipitated in the form of very fine needles when a solution of copper sulphate is added to a soluble salt of the sulphamine acid. When dry, the salt is very light, has a delicate bluish color, and exhibits magnetic properties.

Action of Phosphorus Pentachloride on Parabrombenzoic Sulphinide.

Twenty grams of parabrombenzoic sulphinide were mixed with an equal quantity of phosphorus pentachloride and heated in sealed tubes for five hours at 180°. The product of the reaction was a clear, dark-brown, oily substance, which solidified soon after being poured into cold water. The solid product was filtered off, washed thoroughly, and dried. It had the characteristic odor of nitriles. Five grams of this product were placed in a small, round-bottomed flask containing 30 grams of concentrated sulphuric acid and 10 grams of water, the flask was connected with an upright condenser, and the mixture gently heated until a quantity of needle-like crystals had sublimed in the neck of the flask. The mixture was allowed to cool, when a substance crystallized out in the form of needles. These were collected on an asbestos filter and dissolved in hot water. When the solution cooled, only a small quantity of the product crystallized out. This appeared in the form of needles and proved to be parabromorthochlorbenzoic acid, first made by Willgerodt and Salzmann.[1] The filtrate from these crystals was evaporated to a small volume, and on cooling solidified almost entirely in the form of a crystalline mass. This was found to be parabromorthosulphobenzoic acid, as was proved by neutralizing a portion with potassium hydroxide and adding to the concentrated solution a small quantity of hydrochloric acid. The acid potassium salt was precipitated in small, lustrous plates. Upon analysis, 0.3027 gram salt gave 0.0828 gram K_2SO_4.

	Calculated for  $C_6H_3Br\langle\begin{smallmatrix}COOH\\SO_2OK\end{smallmatrix}$.	Found.
K	12.22	12.27

When the free acid is recrystallized several times it can be obtained in large, rectangular plates, melting at 117°.

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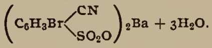
[1] J. prakt. Chem. [2], 39, 470 (1889).

Another portion of the product obtained from the action of phosphorus pentachloride on the brombenzoic sulphinide was subjected to distillation with steam. A product distilled over, having the odor of nitriles and collecting in fine needles. This was proved to be parabromorthochlorbenzoic nitrile by hydrolyzing it in sealed tubes with hydrochloric acid. It was converted into parabromorthochlorbenzoic acid.

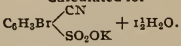
When, in the distillation with steam, the nitrile ceased to come over, the solution in the flask was evaporated to a small volume. On cooling, this solidified into a slightly yellowish, amorphous substance. It was found to give an acid reaction. A portion of it was dissolved in water and neutralized with barium carbonate. The excess of barium carbonate was removed and the clear solution allowed to stand several days. During this time a salt crystallized out in the form of prisms, which, when recrystallized, came out in the same form, and upon analysis proved to be barium parabromorthocyanbenzenesulphonate with 3 molecules of water of crystallization.

0.2824 gram substance lost 0.0212 gram H_2O.
0.2640 gram substance lost 0.0197 gram H_2O.
0.2624 gram substance gave 0.0912 gram $BaSO_4$.
0.2640 gram substance gave 0.0854 gram $BaSO_4$.

	Calculated for	Found.	
	 $\left(C_6H_3Br\begin{array}{l}CN\\SO_2O\end{array}\right)_2Ba + 3H_2O.$	I.	II.
H_2O	7.57	7.50	7.46
Ba	19.11	19.03	19.03

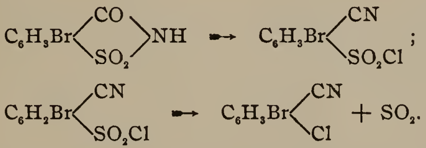
The potassium salt was also made. It was identical with the potassium parabromorthocyanbenzenesulphonate obtained from the corresponding ammonium salt, as has already been described.

0.1537 gram substance lost 0.0128 gram H_2O.
0.1537 gram substance gave 0.0410 gram K_2SO_4.

	Calculated for	
	 $C_6H_3Br\begin{array}{l}CN\\SO_2OK\end{array} + 1\frac{1}{2}H_2O.$	Found.
H_2O	8.25	8.32
K	11.92	11.95

An attempt to obtain the barium salt in the above form from a second lot of the acid did not prove successful. The salt crystallized in needles, and was very soluble in water.

The results of the above experiment indicate quite clearly that when phosphorus pentachloride and parabrombenzoic sulphinide are heated in sealed tubes two products are formed, parabromorthocyanbenzenesulphone chloride and parabromorthochlorbenzoic nitrile. Further investigation proved this to be the case. It was found that when the temperature is not allowed to rise higher than 150°, the main product of the reaction is the bromcyansulphone chloride; when the temperature is raised to 200°, the larger part of the product is bromchlorbenzoic nitrile. The reaction probably takes place in two stages:

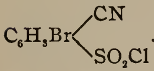


$$C_6H_3Br\left\langle\begin{matrix}CO\\SO_2\end{matrix}\right\rangle NH \longrightarrow C_6H_3Br\left\langle\begin{matrix}CN\\SO_2Cl\end{matrix}\right. ;$$

$$C_6H_2Br\left\langle\begin{matrix}CN\\SO_2Cl\end{matrix}\right. \longrightarrow C_6H_3Br\left\langle\begin{matrix}CN\\Cl\end{matrix}\right. + SO_2.$$

When the tubes that had been heated to 200° were opened there was always present a strong odor of sulphur dioxide.

Parabromorthocyanbenzenesulphone Chloride,



$C_6H_3Br\left\langle\begin{matrix}CN\\SO_2Cl\end{matrix}\right.$.—This compound is easily prepared by heating parabrombenzoic sulphinide with an equal quantity of phosphorus pentachloride in sealed tubes at 150°. It can be separated from the nitrile accompanying it by crystallizing it several times from ligroin. It is readily soluble in hot ligroin, but only slightly soluble in cold. It is very soluble in benzene and glacial acetic acid. When crystallized several times from ligroin it can be obtained in perfectly white plates, having no odor and melting at 82°. When boiled with water it is readily converted into parabromorthocyanbenzenesulphonic acid, and when heated with slightly diluted sulphuric acid it is converted into parabromorthosulphobenzoic acid.

0.2470 gram substance gave 0.2755 gram CO_2 and 0.0296 gram H_2O.

0.1678 gram substance gave 0.1963 gram of a mixture of AgCl and AgBr.

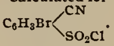
0.1896 gram substance gave 0.2215 gram of a mixture of AgCl and AgBr.

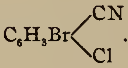
0.2822 gram substance gave 0.01401 gram N.

0.3224 gram substance gave 0.1625 gram N.

0.1678 gram substance gave 0.1422 gram $BaSO_4$.

0.1896 gram substance gave 0.1593 gram $BaSO_4$.

	Calculated for	Found.	
	 $C_6H_3Br<^{CN}_{SO_2Cl}$.	I.	II.
C	29.94	30.41	....
H	1.06	1.33	....
S	11.41	11.63	11.53
N	4.99	4.97	5.04
Cl Br	41.17	40.75	40.70

Parabromorthochlorbenzoic Nitrile,  $C_6H_3Br<^{CN}_{Cl}$.—This compound is readily obtained by heating parabrombenzoic sulphinide with an equal weight of phosphorus pentachloride in sealed tubes at 200°, and distilling the product with steam. The nitrile is volatile with steam and collects in the receiver in the form of fine, white needles. It is very soluble in benzene, glacial acetic acid, and ligroin. The product distilled over with steam, melts at 51° to 61°, and the melting-point is not changed when it is redistilled. When the nitrile is heated either in sealed tubes with hydrochloric acid or in a flask with sulphuric acid containing a little water, it is converted into parabromorthochlorbenzoic acid.

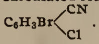
0.2439 gram substance gave 0.3486 gram CO_2 and 0.0324 gram H_2O.

0.2252 gram substance gave 0.3195 gram CO_2 and 0.0278 gram H_2O.

0.2579 gram substance gave 0.0161 gram N.

0.3286 gram substance gave 0.02057 gram N.

0.1885 gram substance gave 0.2850 gram mixture AgCl and AgBr.

	Calculated for	Found.	
	 $C_6H_3Br\begin{smallmatrix}CN \\ Cl\end{smallmatrix}$.	I.	II.
C	38.80	38.08	38.70
H	1.38	1.47	1.37
N	6.46	6.24	6.27
Cl Br	53.34	52.67	....

Summary.

The principal results recorded in the second part of this article may be summed up as follows:

1. When parabromorthocyanbenzenesulphonic acid is boiled with dilute hydrochloric acid, it is not changed. If, however, it is boiled with a slight excess of potassium hydroxide or sodium hydroxide, it is converted into the potassium or the sodium salt of parabromorthocarbaminesulphonic acid.

2. When parabrombenzoic sulphinide is boiled with dilute hydrochloric acid for forty-five minutes, it is converted into parabromorthosulphaminebenzoic acid. When it is boiled with a slight excess of potassium hydroxide for five hours, it is converted into the potassium salt of parabromorthosulphaminebenzoic acid.

3. When the alkali salts of parabromorthocarbaminesulphonic acid are boiled for ten hours with dilute alkalies they are partly converted into the corresponding salts of parabromorthosulphobenzoic acid.

4. When parabromorthosulphaminebenzoic acid is boiled with dilute hydrochloric acid, it is readily converted into the acid ammonium salt of parabromorthosulphobenzoic acid. When it is boiled with a slight excess of potassium hydroxide it is not changed.

5. When parabrombenzoic sulphinide is heated with phosphorus pentachloride in sealed tubes at 150°, the main portion of the product is parabromorthocyansulphone chloride. If the temperature is raised to 200°, the larger proportion of the product is parabromorthochlorbenzoic nitrile.

Contributions from the Chemical Laboratory of Harvard College.

ON THE ACTION OF ANILINE UPON TETRABROMORTHOBENZOQUINONE.[1]

By C. Loring Jackson and Horace C. Porter.

In continuing the work on orthoquinone, begun by Koch and one of us[2] a few years ago, we have studied the action of aniline on the tetrabromorthobenzoquinone, and have found that if the reaction is carried on in alcoholic solution the first product must be dianilinodibromorthoquinone. This substance, however, does not appear as one of the products of the reaction, because of its great tendency to form addition-compounds, so that the first product of the reaction is its compound with aniline,

$$C_6Br_2(C_6H_6NH)_2O_2C_6H_5NH_2,$$

pale-brown needles, melting with decomposition at 121° to 124°, while later there is obtained its compound with alcohol,

$$C_6Br_2(C_6H_5NH)_2O_2C_2H_5OH,$$

yellow plates melting with decomposition at 142°, or, if methyl alcohol is used as a diluent, the corresponding methyl compound, which melts at 144° to 145°. These addition-products are decidedly unstable, the aniline derivative being converted into the alcohol compound by standing for a few minutes with alcohol in the cold. They are also slowly decomposed at temperatures as low as 60°, and by digestion at about 50° with a mixture of benzol and ligroin. They can, on the other hand, be recrystallized from benzol without decomposition, and we ascribe this difference to the fact that the dianilinodibromorthoquinone is but slightly soluble in the mixture of benzol and ligroin, whereas it is freely soluble in benzol alone.[3]

The best method of obtaining the dianilinodibromorthobenzoquinone, $C_6Br_2(C_6H_5NH)_2O_2$, is by repeatedly digesting its aniline compound with a mixture of benzol and ligroin. It crystallizes in dark, reddish-purple needles and melts at 160°. It combines easily with aniline dissolved in benzol, or with ethyl alcohol to form the addition-compounds already described.

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[1] The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University for the degree of Doctor of Philosophy, by Horace C. Porter.

[2] This Journal, **26**, 10 (1901).

[3] Compare the similar phenomena observed by Niemeyer with nitroaniline and chlorquinones. Ann. Chem. (Liebig), **228**, 324 (1885).

The very slight stability of these addition-compounds makes it probable that they are hemiacetals, or the corresponding compound formed by the addition of a molecule of aniline to one carbonyl group, and this view of their constitution is in harmony with the work of Zincke and Arnst,[1] Zincke and Neumann,[2] and Zincke and Schaum,[3] which has proved the existence of hemiacetals derived from other substituted orthoquinones, but, if they are hemiacetals, it is strange that the addition is confined to one of the carbonyl groups. We hope that in the coming year this hypothesis in regard to our substances may be tested experimentally in this laboratory.

If the dianilinodibromorthobenzoquinone or any of its addition-compounds is left standing with a mixture of aniline or an aniline salt and alcohol, or boiled for a few minutes with such a mixture, a new substance is formed crystallizing in very brilliant, jet-black plates and melting at 173°, which proved, on analysis, to be a dianilinobromquinoneanil. This is the substance obtained by Zincke[4] from the action of aniline on tetrabromorthobenzoquinone, but not analyzed by him. As the method of preparation shows, it is much more stable than the compounds previously mentioned in this paper, and is, in fact, the usual product of the reaction of aniline on tetrabromorthoquinone when no special precautions are taken to stop the action at the derivatives of dianilinodibromorthoquinone. The stability of this black compound suggests the idea that it may be a derivative of paraquinone, and this is essentially proved to be the case by the fact that an ethereal solution of sulphurous dioxide converts it in the cold into the known dianilinoparaquinoneanil melting at 202° to 203°. As it is hardly possible to suppose that the change from the ortho to the para series would have taken place under such conditions, we are led to the conclusion that the black substance is already a para compound, and that the action of the sulphurous dioxide has consisted only in the replacement of the atom of bromine by hydrogen—a replacement observed in other cases by Stenhouse[1] and by Earle and one of us.[2] The conclusion that the black compound is a derivative of paraquinone is confirmed by the observation that it shows none of the tendency to form addition-compounds, which is so characteristic of orthoquinones. We can, therefore, safely consider it the dianilinobromparaquinoneanil,

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[1] Ann. Chem. (Liebig), **267**, 319 (1892).

[2] *Ibid.*, **278**, 173 (1894).

[3] Ber. d. chem. Ges., **27**, 537 (1894).

[4] *Ibid.*, **20**, 1778 (1887).

$$C_6HBr(C_6H_5NH)_2ONC_6H_5.$$

Such conversions of ortho- into paraquinones are not rare—Zincke observed them in the action of aniline on β-naphthoquinone,[3] and on chlor- and dichlor-β-naphthoquinone [4](in fact he did not succeed in isolating the β-anilino compounds); Koch and one of us[5] with the chloroform solution of orthobenzoquinone. Liebermann[6] has given a satisfactory explanation of these conversions, which take place, first by the entrance of an anilino group into the ring in the para position to one of the carbonyl groups; second, the hydrogen from this anilino group is transferred to the second carbonyl group forming an oxyparaquinoneanil; and finally, the further action of aniline replaces the hydroxyl by an anilino group. Andersen[7] has prepared a dianilinochlorparaquinoneanil by the action of aniline on trichlorquinonechlorimide, which melts at 195°, a higher temperature than the melting-point of our brom-compound. It may, however, have a different constitution.

If the dianilinobromparaquinoneanil was heated with aniline and alcohol for four hours it was converted into the dianilinoparaquinoneanil,[8]

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[1] Ann. Chem. (Liebig), Supplement, **8**, 20 (1872).

[2] This Journal, **26**, 46 (1901).

[3] Ber. d. chem. Ges., **14**, 1493 (1881) ; *Ibid.*, **15**, 481 (1882).

[4] *Ibid.*, **19**, 2498 (1886).

[5] This Journal, **26**, 33 (1901).

[6] Ber. d. chem. Ges., **14**, 1664 (1881) ; more fully Liebermann and P. Jacobson : Ann. Chem. (Liebig), **211**, 73 (1882).

[7] J. prakt. Chem. [2], **28**, 429 (1883).

[8] Zincke and Hagen : Ber. d. chem. Ges., **18**, 785 (1885).

$$C_6H_2(C_6H_5NH)_2ONC_6H_5,$$

recognized by its melting-point, 202° to 203°, and crystalline form. It follows from this that dianilinodibromorthoquinone or any of its derivatives will also give this compound under the same conditions. The aniline in this case has acted only by replacing the atom of bromine by hydrogen, probably with the formation of tribromaniline; and the atom of bromine must have been replaced in a similar way in the conversion of the dianilinodibromorthoquinone into dianilinobromparaquinoneanil. This furnishes two new examples of the abnormal replacement of bromine by hydrogen, which has been studied for so many years in this laboratory.

The constitution of the dianilinoparaquinoneanil has been settled without much doubt by the following series of transformations: It is converted into azophenin by long heating with aniline at 180° to 200°; azophenin by long boiling with sulphuric acid and alcohol gives aniline and the 2,5-dianilinoquinone.[1] It follows, therefore, that the dianilinoparaquinoneanil has the structure

$$O1,NC_6H_54,(C_6H_5NH)_22,5.$$

As our brom-compound is converted into this so easily, it must have a similar structure with the bromine at either 3 or 6, and consequently one of the atoms of bromine in dianilinodibromorthoquinone is ortho to one of the carbonyl groups, unless, indeed, in the series of reactions for the conversion of the ortho- into the paraquinone one quinone oxygen has been replaced by hydrogen, which is such a strained hypothesis that it seems unworthy of consideration. As it is highly improbable that the dianilinodibromorthoquinone is unsymmetrical, its structure can be safely accepted as

$$O_21,2.Br3,6.(C_6H_5NH)_24,5,$$

and this is the constitution which would have been expected, because, judging from analogy, the atoms of bromine para to the two atoms of oxygen would be most liable to replacement. Kehrmann[2] has shown that in paraquinones two amino groups always enter the molecule in the para position to each other. It would seem from the foregoing considerations that this rule does not apply to orthoquinone.

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[1] O. Fischer and Hepp: Ber. d. chem. Ges., **21**, 2618 (1888).

[2] Ber. d. chem. Ges., **23**, 907 (1890).

Some experiments on the reduction of the dianilinodibromorthoquinone gave products showing the qualitative tests for pyrocatechin, but owing to lack of time they were not studied thoroughly.

We also include in this paper the description of some work upon the reduction-product from hexabromorthoquinopyrocatechin ether. Koch and one of us[1] found that this substance did not dissolve in sodic hydrate, and there seemed some doubt, therefore, as to whether it really was the expected diatomic phenol. We have now proved that it contains the hydroxyl group, since treatment with benzoyl chloride converted it into a monobenzoic ester,

$$C_6Br_4O_2C_6Br_2OHOCOC_6H_5,$$

a white, crystalline body. We obtained indications that a dibenzoic ester could be obtained by the Baumann-Schotten method, but as the monobenzoic ester had settled the point in question we did not try to isolate the dibenzoic ester.

EXPERIMENTAL PART.

The tetrabromorthobenzoquinone used in this work was prepared by the method of Zincke,[2] that is the oxidation of tetrabrompyrocatechin dissolved in glacial acetic acid, with fuming nitric acid also diluted with glacial acetic acid. The details of this preparation are given in the paper by Koch and one of us.[3] We have to add to what is said there, that it is important to filter off the tetrabromorthoquinone with the least possible delay, as it decomposes rapidly if left in contact with the oxidation solution. The quinone should not be dried at temperatures above 70°, as it decomposes when heated above that point. Our yields were somewhat better than those obtained by Koch and one of us: From 20 grams of pyrocatechin we obtained from 60 to 70 grams of tetrabrompyrocatechin in place of 59 to 63 grams, and 30 grams of the tetrabrompyrocatechin gave 21 grams of tetrabromorthoquinone, a yield of 70 per cent of the theory instead of the 60 per cent in the earlier work. As before, the tetrabromorthoquinone was used without recrystallization, because this was such a wasteful process owing to the action of almost all solvents on it. The substance used by us melted at 145° to 146° instead of 150° to 151°.

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[1] This JOURNAL, 26, 36 (1901).

[2] Ber. d. chem. Ges., 20, 1777 (1887).

[3] This JOURNAL, 26, 34 (1901).

Reduction of the Hexabromorthoquinopyrocatechin Ether, $C_6Br_4O_2C_6Br_2O_2$.

In the previous paper by Koch and one of us[1] this reduction was described, and some account of the product was given. Since, however, it was insoluble in sodic hydrate it did not seem certain that this product contained two hydroxyl groups, as was indicated by the ease with which it passed back to the original (quinone) substance by oxidation. We have therefore taken up again the study of this substance, as upon its nature rests the constitution of the hexabromorthoquinopyrocatechin ether.

The red ether for these experiments was prepared by the method of Koch and one of us, that is to a solution of 11 grams of tetrabromorthoquinone and 10 grams of tetrabrompyrocatechin in 470 cc. of glacial acetic acid 180 cc. of water were added, and the mixture allowed to stand twenty-four hours in a warm place. The red precipitate thus formed was filtered out and washed thoroughly with hot alcohol. In this way 12.5 to 13 grams were obtained, that is about 72 per cent of the theoretical yield. The reduction of the ether was carried on as before.[2] Five grams of the red hexabromorthoquinopyrocatechin ether suspended in water were exposed to the action of sodium amalgam for two or three days in a flask, which was kept filled with carbonic dioxide. The product, which had changed from red to white, was filtered out, and turned to a dull-purple color on exposure to the air. It was washed with dilute acetic acid, water, and alcohol, dried at 100°, and purified by crystallization from hot nitrobenzol.

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[1] This JOURNAL, **26**, 38 (1901).

[2] *Ibid.*, **26**, 38 (1901).

The solvent should not be raised to its boiling-point, as this causes a decomposition of the substance. The pure compound, which we found melts at 304° to 307°, was dried at 100°, and analyzed with the following result:

0.2398 gram substance gave 0.1885 gram CO_2 and 0.0133 gram H_2O.

	Calculated for $C_{12}Br_6(OH_2)O_2$.	Found.
C	20.87	21.44
H	0.29	0.62

The properties of the substance agreed with those previously observed except that the crystals from nitrobenzol appeared as iridescent scales instead of short needles. An aqueous solution of sodic hydrate does not dissolve it, as observed in the earlier work, but turns it dark-purple. An alcoholic solution of sodic hydrate seems to decompose it very thoroughly, as oxalic acid was the only product recognized.

Action of Benzoyl Chloride on the Reduction-product.

In order to obtain the object of this work—the testing of the body for hydroxyl groups—we next treated it with benzoyl chloride. One gram of the purplish crystals of the reduced substance was moistened with 2 to 3 cc. of benzoyl chloride and warmed gently till the reaction had started, as shown by effervescence. On cooling, the whole solidified to a pulpy mass of white crystals, which was warmed twice more with fresh portions of benzoyl chloride in order to complete the reaction. The crystals thus obtained were treated with a large amount of hot alcohol, washed with hot alcohol, and recrystallized twice from hot nitrobenzol, after which they were washed with alcohol, dried at 100° and analyzed with the following result:

0.1483 gram substance gave, by the Carius method, 0.2095 gram AgBr.

	Calculated for $C_{12}Br_6O_2(OH)(OCOC_6H_5)$.	Found.
Br	60.45	60.12

There can be no doubt, therefore, that the substance is a monobenzoyl derivative of the reduced substance, which, therefore, contains hydroxyl groups. The yield was good, as from 1 gram of the original substance 0.6 gram of the benzoic ester, purified by recrystallization, was obtained. Attempts to make the dibenzoyl compound by the Baumann-Schotten method gave mixtures of varying composition.

Properties of the Monobenzoyl Ester of the Hexabromorthodioxypyrocatechin Ether.—It is a white, crystalline substance melting at 316° to 318°. It is essentially insoluble in the common solvents, although very slightly soluble in benzol or acetone; soluble in nitrobenzol, which is the best solvent for it.

Action of Hydrobromic Acid on the Hexabromorthoquinopyrocatechin Ether.

The behavior of the ether with hydrobromic acid was analogous to that with hydrochloric acid, already observed by Koch and one of us.[1] Five-tenths gram of the red ether was heated in a sealed tube to 100°, for twenty-four hours, with 5 to 6 cc. of distilled hydrobromic acid (boiling at 126°). The products were bromine, recognized by its smell, and the formation of a blue color with potassic iodide and starch, a purplish solid looking like the reduction-product with sodium amalgam, not melting below 300°, and converted by nitric acid into the original red ether—properties which identify it as the hexabromorthodioxypyrocatechin ether—and a white, crystalline substance, soluble in hot water and recognized as a substituted pyrocatechin by the green color-test with ferric chloride. The amount of this latter body was not very great, but by oxidizing the reduction-product with nitric acid and heating again with hydrobromic acid more of it was obtained, so that it was evident that a sufficient number of such treatments would convert the ether completely into this substituted pyrocatechin (probably tetrabrompyrocatechin). In this respect the hydrobromic acid reduction was entirely analogous to the reduction with sodium amalgam described by Koch and one of us.

Action of Aniline on Tetrabromorthoquinone.

After a number of experiments we found that the anilino derivatives of tetrabromorthoquinone were most conveniently prepared as follows: A solution of 5 grams of tetrabromorthoquinone in 100 cc. of alcohol was added to a cold mixture of 7.5 grams of aniline and 100 cc. of alcohol, in small portions at a time, with vigorous stirring. A light-brown, very bulky precipitate formed at once, which rendered the liquid so pasty by the time half the quinone had been added that it was best to filter out the precipitate with the pump and continue the addition of the rest of the quinone to the filtrate. Upon stirring the mixture of quinone and the filtrate, a yellow body crystallized out in the track of the rod on the sides of the beaker, and the light-brown substance at first mentioned was converted into this same yellow compound if it was allowed to stand in contact with the liquid for half an hour or less. The alcoholic filtrate from the yellow crystals, if allowed to stand over night at ordinary temperatures, or if boiled for a few minutes, deposited lustrous, black crystals of a third compound, but, if the filtrate was boiled for about four hours, it formed reddish-brown crystals of the dianilinoparaquinoneanil. Of the four products obtained from this reaction, the last two are derivatives of parabenzoquinone. The first two are derivatives of dianilinodibromorthobenzoquinone, and it will be well, therefore, to describe this compound before considering its derivatives.

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[1] This JOURNAL, 26, 40 (1901).

Dianilinodibromorthobenzoquinone, $C_6Br_2(C_6H_5NH)_2O_2$.–This substance was most conveniently made from the pale-brown, voluminous precipitate, which formed the first product of the action of aniline in alcoholic solution on the tetrabromorthoquinone (see the preceding section). This is an addition-compound of the dianilinodibromorthoquinone and aniline. To remove the additional aniline, the precipitate was allowed to dry at ordinary temperatures to get rid of the adhering alcohol, and then heated to about 50° with a mixture of 5 parts of benzol and 1 part of ligroin. After heating for a few minutes, the substance had changed from pale-brown to reddish-purple, the solid was then filtered out and digested in the same way with a fresh quantity of the mixture of benzol and ligroin, and these digestions with fresh portions of the mixed solvents were repeated three or four times, after which the substance was purified by crystallization from the boiling benzol and ligroin mixture (5 : 1) until it showed the constant melting-point 160°. The first benzol and ligroin filtrates obtained in this process deposited some of the pale-brown addition-compound on standing and contained aniline. The substance melting at 160° was dried at 100° and analyzed with the following results :

I. 0.3216 gram substance gave 17.2 moist N at 16° and 776 mm. pressure.

II. 0.2054 gram substance gave, by the Carius method, 0.1717 gram AgBr.

III. 0.2447 gram substance gave 0.2063 gram AgBr.

	Calculated for $C_6Br_2(C_6H_5NH)_2O_2$.	Found. I.	II.	III.
N	6.25	6.29	....	....
Br	35.71	....	35.57	35.88

Properties of Dianilinodibromorthobenzoquinone.—It crystallizes from benzol in pointed needles of a dark, reddish-purple color. It melts at 160°, and is easily soluble in benzol, glacial acetic acid, or acetone ; slightly soluble in alcohol or ether ; very slightly soluble in ligroin. The best solvent for it is a boiling mixture of benzol and ligroin. Strong hydrochloric acid has almost no effect upon it. Strong nitric acid dissolves it with decomposition ; strong sulphuric acid dissolves it with a yellowish-green color ; hot sodic hydrate solution dissolves it with decomposition. Tin and hydrochloric acid, or a solution of sulphurous acid, reduces it easily to a substance giving tests for pyrocatechin. Its most striking property is the ease with which it forms addition-compounds with aniline or alcohols, some of which are described in the following sections.

Addition-compound of Aniline and Dianilinodibromorthoquinone, $C_6Br_2(C_6H_5NH)_2O_2C_6H_5NH_2$.—This substance is the pale-brown precipitate formed at first by the action of aniline on tetrabromorthoquinone in alcoholic solution. For analysis it was purified by two crystallizations from boiling benzol. This method of purification seems strange when it is remembered that the body is decomposed into aniline and dianilinodibromorthoquinone by treatment with benzol and ligroin at 50°. The most probable explanation is that the product is decomposed by solvents in which the dianilinodibromorthoquinone is only slightly soluble, whereas solutions in benzol and similar solvents, in which the quinone is freely soluble, deposit the unaltered addition-compound. For analysis, it was dried *in vacuo.*

I. 0.1970 gram substance gave, on combustion, 0.3868 gram CO_2 and 0.0700 gram H_2O.

II. 0.2502 gram substance gave, by the Carius method, 0.1731 gram AgBr.

	Calculated for $C_6Br_2(C_6H_5NH)_2O_2C_6H_5NH_2$.	Found.	
		I.	II.
C	53.23	53.56	....
H	3.51	3.95	....
Br	29.57	....	29.45

The results of this analysis are confirmed by the following observations: In converting the addition-compound into dianilinodibromorthoquinone by digestion with benzol and ligroin, the filtrates were found to leave a residue of aniline on evaporation. The aniline was recognized by giving a soluble chloride, the isonitrile reaction with chloroform and potassic hydrate, and forming again the addition-compound when treated with tetrabromorthoquinone. The addition-compound is also easily made by boiling the dianilinodibromorthoquinone with the calculated amount of aniline dissolved in benzol.

Properties of $C_6Br_2(C_6H_5NH)_2O_2C_6H_5NH_2$.—It crystallizes from boiling benzol in pale-brown, long, fine needles. It begins to lose aniline if warmed for some time at 50° to 60°, but the product does not seem to be the dianilinodibromorthoquinone, apparently because the aniline acts further upon it at this temperature. If heated rapidly, it melts with decomposition between 121° and 124°. The slight stability of the substance is also shown by its complete decomposition by the action of a solvent-like benzol and ligroin (5 : 1), in which the dianilinodibromorthoquinone is only slightly soluble. It is also decomposed by hot glacial acetic acid, or even by boiling with water. It is freely soluble in alcohol, benzol, or acetone, although the alcohol solution gradually decomposes in the way described in the next section; slightly soluble in ether or ligroin. Strong hydrochloric acid decomposes and dissolves it (difference from the dianilinodibromorthoquinone); strong nitric acid also dissolves it with decomposition; strong sulphuric acid dissolves it with a yellowish-green color; hot sodic hydrate solution dissolves it with decomposition.

Addition-compound of Dianilinodibromorthobenzoquinone with Ethyl Alcohol, $C_6Br_2(C_6H_5NH)_2O_2C_2H_5OH$.—The yellow precipitate formed during the action of aniline and alcohol on tetrabromorthoquinone was this body. It was also easily obtained by moistening the dianilinodibromorthoquinone or its aniline addition-compound with ethyl alcohol, and allowing the mixture to stand for several days. It was purified by crystallization from warm benzol, care being taken that the temperature did not rise above 50°. After two such recrystallizations it was dried *in vacuo* and analyzed with the following results:

I. 0.3604 gram substance gave 19.2 cc. moist N at 18° and 768 mm. pressure.

II. 0.1644 gram substance gave, by the Carius method, 0.1247 gram AgBr.

III. 0.1717 gram substance gave 0.1294 gram AgBr.

IV. 0.1548 gram substance gave 0.1175 gram AgBr.

V. 0.2167 gram substance gave 0.1647 gram AgBr.

	Calculated for	Found.				
	$C_6Br_2(C_6H_5NH)_2O_2C_2H_5OH$.	I.	II.	III.	IV.	V.
N	5.67	6.22	....	....	....	....
Br	32.39	....	32.28	32.08	32.32	32.34

For greater certainty the amount of ethyl alcohol in it was determined by Zeisel's method[1] with the temperature of the baths modified to correspond with ethyl iodide.

0.3124 gram substance gave, by Zeisel's method, 0.1608 gram AgI.

	Calculated for $C_6Br_2(C_6H_5NH)_2O_2C_2H_5OH$.	Found.
OC_2H_5	9.11	9.83

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[1] Monatsh. Chem., **6**, 986; **7**, 406; or Sitzber. Akad. Wiss. Wien., **92** [2], 1431; **94** [2], 341.

Properties of $C_6Br_2(C_6H_5NH)_2O_2C_2H_5OH$.—It crystallizes from benzol in bright-yellow plates of about the color of plumbic chromate. These plates are oblong and nearly rectangular, but careful observation shows that the short sides consist of two planes at a reentering angle so obtuse that they might easily be mistaken for a straight line. If heated rapidly, it melts fairly constantly at 142°, but this melting is accompanied by decomposition, as the substance turns black and increases in volume. The melting-point, therefore, is much influenced by the length of the heating, and is the same only when care is taken to make the conditions the same. The substance decomposes by long heating at temperatures far below its melting-point, and this decomposition was studied as follows: About 0.3 gram of the body, carefully dried in a current of air and *in vacuo*, was heated in a small test-tube provided with a narrow air-condenser dipping under a few drops of water. After heating to 110° to 125° for nearly three hours, drops of a colorless liquid were observed in the condenser. These were washed out with very little water and tested with iodine and potassic hydrate for ethyl alcohol. The presence of iodoform was established by the yellow color and the odor, so there can be no doubt that alcohol had distilled off. The solid residue in the test-tube was blackened and partially fused, and after one crystallization from the mixture of benzol and ligroin (5 : 1) melted at a higher temperature (150° to 160°) than the original substance. We did not attempt to isolate the dianilinodibromorthoquinone from it.

In a second experiment, the temperature was kept at 90° to 95°, and the substance heated in a watch-glass to determine the amount of alcohol given off. The weighings were taken at intervals of two or three hours, and showed a fairly rapid loss for the first twenty-three hours, when it amounted to 9.8 per cent. If $C_6Br_2(C_6H_5NH)_2O_2C_2H_5OH$ loses the 1 molecule of ethyl alcohol, the loss would be 9.31 per cent. After the twenty-third hour, the amount of loss in three hours diminished to a very marked extent, but continued heating caused a slight additional loss up to forty-eight hours, when the experiment was stopped. It seems, therefore, that the alcohol is given off fairly rapidly and completely even at this low temperature, and that this escape of the alcohol is accompanied by a gradual decomposition of the residual quinone. A loss of alcohol from this substance was observed even at 60°.

The substance dissolves very freely in acetone; it is moderately soluble in alcohol, ether, or benzol; very slightly soluble in ligroin. Hot glacial acetic acid dissolves it with decomposition, shown by the dark-purple color of the solution, and it is also decomposed by continued boiling of its solutions, as would be expected when the slight stability of the substance toward heat is remembered. A boiling mixture of benzol and ligroin (5 : 1) is especially well adapted to bring about this change. Strong hydrochloric acid dissolves it, and aqueous sodic hydrate, when hot, has the same effect.

Addition-compound of Dianilinodibromorthobenzoquinone and Methyl Alcohol, $C_6Br_2(C_6H_5NH)_2O_2CH_3OH$.—This substance was made by the action of aniline on tetrabromorthoquinone dissolved in methyl alcohol. This method of preparing it is better than moistening the dianilinodibromorthoquinone with methyl alcohol, as in that case the product dissolves in the methyl alcohol.

0.2902 gram substance gave, by the Carius method, 0.2269 gram AgBr.

	Calculated for $C_6Br_2(C_6H_5NH)_2O_2CH_3OH$.	Found.
Br	33.33	33.28

It resembles the corresponding ethyl compound in most respects, but has a somewhat lighter yellow color, and melts with decomposition at 144° to 145°, that is a few degrees higher than the ethyl alcohol addition-product.

Dianilinobromparaquinoneanil, $C_6HBr(C_6H_5NH)_2ONC_6H_5$.—This is the product most easily obtained by the action of aniline on tetrabromorthoquinone, as it is stable enough to require in its preparation no particularly careful attention to detail, such as is necessary in making the orthoquinone compounds just described, and, further, all these orthoquinone derivatives are converted easily into this dianilinobromparaquinoneanil.

It was most easily prepared by the method given under the heading, Action of Aniline on Tetrabromorthoquinone, that is by allowing the alcoholic filtrate from the aniline addition-compound of dianilinodibromorthoquinone to stand for several hours, or more quickly by boiling it for a few minutes. Other methods of preparation were: Boiling dianilinodibromorthoquinone or its addition-compounds with alcohol and a little aniline for a short time. Adding aniline to a cold benzol solution of tetrabromorthoquinone, when a precipitate was formed consisting of the aniline addition-compound of dianilinodibromorthoquinone and aniline chloride. On boiling this precipitate with a mixture of alcohol and benzol it was converted into the dianilinobromparaquinoneanil. Finally, by adding aniline to a boiling solution of tetrabromorthoquinone in alcohol or in glacial acetic acid. It was purified by recrystallization from a boiling mixture of equal parts of benzol and methyl alcohol until it showed the constant melting-point 173°, when it was analyzed with the following results:

I. 0.1198 gram substance gave, on combustion, 0.2875 gram CO_2 and 0.0509 gram H_2O.

II. 0.3685 gram substance gave 31.5 cc. moist N at 26°.5 and 772 mm. pressure.

III. 0.2422 gram substance gave, by the Carius method, 0.1027 gram AgBr.

	Calculated for $C_6HBr(C_6H_5NH)_2ONC_6H_5$.	Found. I.	II.	III.
C	64.86	65.45	....	....
H	4.05	4.72	....	....
N	9.46	....	9.59	....
Br	18.02	....	....	18.04

The molecular weight was also determined by the freezing-point method in benzol.

I. 0.2811 gram substance, in 20 grams benzol, produced a depression $\varDelta = 0°.185$.

II. 0.1245 gram substance produced a depression $\varDelta = 0°.073$.

	Calculated for $C_6HBr(C_6H_5NH)_2ONC_6H_5$.	Found. I.	II.
Mol. wt.	444	372	418

These results leave no doubt as to the formula of the compound. Our reason for assigning it to the para rather than the ortho series is that an ethereal solution of sulphurous dioxide in the cold converts it into the known dianilinoparaquinoneanil, and it seems improbable that a passage from the ortho to the para group could take place under such conditions. This conclusion is supported by the fact that it does not show the strong tendency to form addition-products, which is so characteristic of the orthobenzoquinone derivatives. The mechanism of the change from the ortho to the para compound is discussed in the introduction to this paper.

Properties of Dianilinobromparaquinoneanil.—It crystallizes from a mixture of benzol and alcohol in jet-black plates with an uncommonly brilliant luster. Thin plates, under the microscope, have a dark yellowish-brown color, which becomes black when the plate is of ordinary thickness. The plates are shaped like spear-heads, that is they have a sharp, rhombic form with a slight reentering angle on each side. Its melting-point was found to be 173°. It is freely soluble in benzol, glacial acetic acid or acetone; moderately soluble in ethyl or methyl alcohol or in ether; it is decomposed by recrystallization from alcohol; very slightly soluble in ligroin. The best solvent for it is a mixture of equal parts of benzol and methyl alcohol. Hot, strong hydrochloric acid dissolves it slowly with a greenish color; strong nitric acid dissolves it with decomposition; strong sulphuric acid dissolves it with a dark purplish-red color, which distinguishes it from the ortho compounds described earlier in this paper, as these impart a greenish-yellow color to strong sulphuric acid. Sodic hydrate has no apparent effect on it, hot or cold. Ether saturated with sulphurous dioxide decolorizes it and deposits crystals of dianilinoparaquinoneanil. The same change is brought about by boiling it for some time with aniline or chloride of aniline and alcohol, and probably more slowly by boiling with alcohol alone. A sample moistened with methyl alcohol, after standing for several weeks, had the melting-point of the original substance, showing that it does not form addition-compounds.

Formation of Dianilinoparaquinoneanil, $C_6H_2(C_6H_5NH)_2ONC_6H_5$.—As has been already stated, this substance, discovered by Zincke and Hagen[1] in 1885, was the final product of the action of aniline on tetrabromorthoquinone in alcoholic solution. We have obtained it in the course of our work in the following ways: Boiling for four hours, the alcoholic filtrates from the preparation of the aniline addition-compound of dianilinodibromorthoquinone; boiling any of the orthoquinone derivatives described in this paper with alcohol and aniline for several hours; boiling the dianilinobromparaquinoneanil with aniline and alcohol for several hours; or treating it in the cold with a saturated ethereal solution of sulphurous dioxide.

The identification of this substance gave us a great deal of trouble. The pure substance melts, according to Zincke and Hagen, at 202° to 203°, but after many recrystallizations from a mixture of equal parts of benzol and alcohol we could not raise the melting-point of our preparations above 199°. Finally, however, by repeated crystallization from methyl alcohol, we succeeded in eliminating the impurity and raising the melting-point to 202° to 203°. To establish the identity of our substance beyond doubt it was compared with some dianilinoparaquinoneanil made from paraquinone by the method of Zincke and Hagen. This, like our specimen from the tetrabromorthoquinone, melted obstinately at about 199°, and could be raised to its true melting-point only with great difficulty. On comparing the two specimens, the only difference observed was a slight one in color, our specimen was purple, that made by Zincke and Hagen's method dark-brown. The crystalline habit of the two was exactly alike. From a mixture of benzol and alcohol both deposited, at first, two slender needles, crossing almost, but not quite, at a right angle. These two needles then became crossed by a large number of shorter needles, apparently at right angles to the main needle, and lying as close together as the teeth of a comb—a very characteristic form. From alcohol alone both gave bunches or sheaves of very long, fine needles. There can be no doubt, therefore, that our substance is the dianilinoparaquinoneanil. We may add that it formed no addition-compound with methyl alcohol even after standing with it for several weeks.

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[1] Ber. d. chem. Ges., 18, 787 (1885).

Reduction of Dianilinodibromorthoquinone.

Our experiments in this direction were left in an unfinished state because of the pressure of other more important work. We think it best, however, to give a brief statement of the results obtained, and hope that this branch of the work will be continued in this laboratory in the near future.

Tin and hydrochloric acid reduced the ethyl alcohol addition-compound of the dianilinodibromorthoquinone to a white body, which we did not succeed in purifying, but which gave tests for a pyrocatechin with plumbic acetate and ferric chloride.

Sulphurous dioxide reduces tetrabromorthoquinone to tetrabrompyrocatechin, either in aqueous or ethereal solution, apparently quantitatively. With dianilinodibromorthoquinone, the aqueous solution of sulphurous dioxide turned yellow, and left, on evaporation, a partially crystalline residue, which gave a test for a pyrocatechin with ferric chloride, but the yield was exceedingly small, as the greater part of the quinone was left unaltered.

Sulphurous dioxide in ethereal solution yielded more promising results. A saturated solution of dianilinodibromorthoquinone in anhydrous ether (dried over sodium) was saturated with sulphurous dioxide, when, on standing, rosettes of dark-green needles separated on the walls of the vessel. As it was too unstable to admit of recrystallization, the crystals were purified by washing with ether. Upon repeating this experiment we did not succeed in obtaining this green substance again, and have not yet been able to give the time necessary to discover the proper conditions for preparing it with certainty. It forms rosettes of small, green needles, which melt at 186° to 188°. It is decidedly unstable, as, when heated, it turns dark-red, and solution in alcohol produces the same change of color. The green color, the instability, and the easy conversion into a red body all point to its being formed by the reduction of part of the quinone to a pyrocatechin, which then combines with some of the unreduced quinone to form a substance analogous to quinhydrone. The substance dried *in vacuo* gave the following result on analysis:

0.1644 gram substance gave, by the Carius method, 0.0834 gram AgBr.

	Calculated for $C_6HBr(C_6H_5NH)_2O_2C_6HBr(C_6H_5NH)_2(OH)_2$.	Found.
Br	21.62	21.59

$C_6HBr(C_6H_5NH)_2O_2$ contains 21.68 per cent of bromine.

Our results are obviously insufficient to establish the nature of this substance with certainty, which must be left to future experiments.

If common (undried) ether was used, a different result was obtained. A saturated solution of dianilinodibromorthoquinone in commercial ether was saturated with sulphurous dioxide and allowed to stand at ordinary temperatures. After twelve hours it had deposited a considerable amount of a white body in long, fine needles, and about one-tenth as much of dark-colored crystals, in which three different forms were recognized—large, amber-colored needles in feather-like aggregations; minute, dark-colored, hexagonal plates; and blunt, rounded needles crossing at an angle of about 60°. These three substances were present in such small quantities that only a qualitative study could be made of them. They dissolved easily in alcohol, and the solution gave a heavy, white precipitate with plumbic acetate, which was soluble in acetic acid. They also gave a deep-green color with ferric chloride. From these observations we infer that one or more are substituted pyrocatechins. The amber-colored needles melted (impure) from 160° to 163°.

The white substance, which was the principal product of the reaction, was roughly separated from the dark crystals by decantation, and crystallized from a mixture of alcohol and ether (1 : 3). It formed long, white needles and was decidedly stable for a substance of this group. It did not melt below 300° and was slightly soluble in cold water, more easily in hot; very freely soluble in methyl or ethyl alcohol; almost insoluble in ether or benzol. Its aqueous solution gave a precipitate with argentic nitrate, and the substance could be salted out of its aqueous solution with salt or hydrochloric acid. Very dilute sodic hydrate dissolved it, giving a clear, greenish solution; cold, strong sodic hydrate seemed to have no action on it, but when hot decomposed it. All these properties indicate that it is a bromide. Its alcoholic solution gives a slight precipitate with plumbic acetate, and ferric chloride imparts a slight green color to it, so that it may be a pyrocatechin. Unfortunately, we did not succeed in purifying it thoroughly for analysis, three different samples giving the following percentages of bromine, 35.11, 37.01, 37.81, so that we can make no definite statement about its composition. It seems possible, however, that it is a pyrocatechin ether derivative, as $C_6Br_2(C_6H_5NH)_2O_2C_6(C_6H_5NH)_2(OH)_2 2HBr$ contains 35.56 per cent of bromine; but, on the other hand, it is hard to bring the formation of such an ether into harmony with the most probable structure for the dianilinodibromorthoquinone, $O_2 1,2.(C_6H_5NH)_2 4,5.Br 3,6$. The more thorough study of this interesting substance will be taken up in this laboratory in the near future.

Attempts to prepare analogous pyrocatechin ethers from pyrocatechin or tetrabrompyrocatechin by the action of sulphurous dioxide in ethereal solution led to no result.

The hexabromorthoquinopyrocatechin ether, when treated with aniline, gave the same products as the tetrabromorthoquinone.

A BUNSEN MEMORIAL.

A movement is on foot to erect a suitable memorial in honor of Robert Bunsen in Heidelberg, where he lived and labored for nearly half a century. The arrangements are in charge of Professor Curtius, who is aided by a large committee of prominent chemists in Europe and America. This country is represented by Professors Jackson, Michael, and Nef.

It is hoped that all former students and friends of Bunsen will show their interest in the work by subscribing to the fund which is being raised. Professor C. Loring Jackson, Cambridge, Mass., has consented to act as treasurer for the American fund, and all subscriptions should be sent to him.

REVIEWS.

Chemical Exercises for Classroom and Home Study. By Rufus P. Williams, Teacher of Chemistry in the English High School, Boston, and Author of Elements of Chemistry, Chemical Experiments, etc. Boston: Ginn & Co. 1903.

These exercises are printed as headings on a letter-pad. The space below and on the reverse of the leaf is to be filled by the student. The leaves are detachable. There are 100 exercises covering inorganic chemistry as commonly taught in the first year of a college course. The questions are admirably chosen, and the result of the use of the exercises must be beneficial. E. R.

A Text-book of Quantitative Chemical Analysis. By Frank Julian. Illustrated. First Edition. St. Paul, Minn.: The Ramsay Publishing Co. pp. 604.

Of the five parts into which the subject matter of this volume is divided, the first deals with the general principles which underlie the methods of quantitative analysis, and the operations which are common to all analyses. It is divided into nine chapters, including those upon methods of sampling, the purchase and care of balances and weights, the processes of solution, evaporation, precipitation, filtration, and the like, the principles of volumetric and gas analysis, "attributive methods," and calculation of analyses, and a discussion of errors and precautions.

Part 2 comprises a detailed description of twenty-four practice exercises in analysis, including such substances as alcohol, coffee, standard acid and alkali, vinegar, chloral hydrate, hydrastis, standard permanganate, forge scale, chrome yellow, metol, galena, lard, air, and wollastonite.

Part 3 is devoted to special methods and technical analysis, the former including the processes of colorimetry, fire assay, electrolysis, ultimate and proximate organic analysis, and chlorimetry, which are applied, among other instances, to irons and steels, iron ores, coal, natural waters, fertilizers, the alcohols and alkaloids, tannins, carbohydrates, oils, fats, soaps, milk, butter, urine, and the organic dyestuffs.

Part 4 contains more "notes and observations relating to the principles and practice of the art in general that may be of interest to the student," and an appendix presents a still further discussion of "certain phases of the important subject of the practice of technical and industrial chemical analysis." The appendix also contains tables and an index.

The author, in his preface, states that the volume is intended to aid students who can devote but a limited time to the study of quantitative analysis, and that he deems it wise to present a "general view of the art as practised at this time," for which purpose he avoids minutely detailed directions, as far as possible, giving greater prominence to underlying principles, in order that the student may, thereby, obtain a broader view and "a more comprehensive knowledge of the art than is afforded by the study of a string of detailed recipes, however practically useful they may be." The volume is also intended as an "introduction to monographs on special departments of technical analysis."

In pursuance of the purpose thus outlined, the author has brought together a mass of material which has involved much careful thought and compilation, and contains a great deal of useful suggestion and sound advice, which cannot fail to be of great value to the student (or the general reader) provided he has the patience and perseverance to ferret it out of the 600 or more pages of inexcusably fine print. That the idea of laying stress upon principles of general application as well as upon the details and the technique of manipulation is sound, no good teacher of analytical chemistry will question. It would seem, however, that in this text-book the author has enunciated general principles at such great length, and has substituted general statements for vital details to such an extent, that the book falls short of furnishing effective aid to either student or practising analyst; because, in a large number of instances no references are given which enable the reader to turn to original sources of information regarding the processes mentioned. So far as such references are given, however, assuming that a chemical library is at the command of the reader, this volume may be found useful, in that it furnishes a general discussion of the methods in use for a particular purpose.

The author's pen moves freely and he has allowed himself almost unlimited space in the expression of his ideas. As a result there is considerable repetition (especially of material in Parts 1, 4, and the appendix) and the force of many statements is likely to be lost upon the student because of their lengthy presentation. It is hardly conceivable that the beginner will be able to assimilate the directions and advice included in 201 pages of fine print, and he will find it difficult to sift out of these pages the vital points.

The intermingling of proximate and ultimate methods of analysis in the exercises for practice, a part of which are enumerated above, is unusual and seems to present difficulties of manipulation and of interpretation of results, which would be confusing to the beginner even though he is asked to make a "determination of the atomic weight of chlorine" as his third exercise. The weighing of ammonium sulphate (p. 221) as a representative method for the standardization of a sulphuric acid solution does not appear to be a fortunate choice, and the use of phenolphthalein as an indicator without making any provision for the presence of carbonate in the caustic soda (p. 223) is inaccurate. The statement (p. 192) that weighing to the nearest milligram is, in general, sufficiently exact will hardly hold true in practice where the analyst is often compelled to work with a small weight of material, and the qualifying statement will hardly safeguard the student from gaining an erroneous impression. The statement (p. 103) that crucibles need not be cooled in a desiccator after ignition, if weighed as soon as cool, seems to take no account of the condensation of moisture on the surface of the crucible itself, and that this may vary in amount from hour to hour.

It is, perhaps, a minor criticism that the use of such words as "succussion" for bumping, "encysted" for enclosed, "extrinsic" for outside, and "plications" for folds, seems cumbrous in a scientific treatise for beginners. The substitution of "preventative" (p. 193) for preventive is, doubtless, an accident of proof-reading, to which may also be attributed the large number of badly printed symbols throughout the volume.

The volume contains a great deal that is of interest and value to analysts, and, while its success as a text-book for beginners, if used alone, may be somewhat problematical, it may well serve a useful purpose for teachers and practising analysts as a reference book in conjunction with other works.

H. P. T.

HANDBOOK OF TECHNICAL GAS-ANALYSIS. By CLEMENS WINKLER, PH.D., Professor of Chemistry at the Freiberg Mining Academy. Second English Edition. Translated from the Third German Edition, with some Additions, by GEORGE LUNGE, PH.D., Professor of Technical Chemistry in the Federal Polytechnic School, Zurich. London: Gurney & Jackson. 1902. pp. 190.

The present translation of Winkler's Technical Gas-Analysis appears as an important and opportune contribution to the literature of gas-analysis. Professor Lunge states in his preface that although the book is published as the second English edition, it really represents the third German edition of Winkler's work. The general arrangement of the book is the same as in the preceding edition, from which it differs mainly by presenting a more thorough and detailed discussion of known reactions in the light of recent literature, rather than by material additions of new methods. A chapter is devoted to the collection and preservation of gas samples. In the second and third chapters are considered the commonly used methods of gas-measurement, the determination of the specific gravities of gases, and the various rapid methods of analysis devised by Winkler, Hempel, and Lunge. Special methods are discussed for the determination of carbon dioxide in air, the determination of fire-damp in the air of mines, and for the examination of gases resulting in various chemical manufacturing operations. Some useful tables follow. The solubility of gases in water and other liquids over which they are measured has always presented a serious obstacle to the satisfactory utilization of many reactions which are noted for their sharpness and adaptability to gasometric methods. Although in an indirect manner and without special reference to this always present difficulty, Winkler offers many useful suggestions for overcoming errors incidental to gasometric work, and presents a brief but excellent treatise. Chemists will find this a valuable book. F. C. P.

PRINCIPLES OF DYEING. By G. S. FRAPS, PH.D., Sometime Fellow, Johns Hopkins University, Assistant Professor of Chemistry, North Carolina College of Agriculture and Mechanic Arts. pp. xii + 270, with 22 illustrations in the text. New York: The Macmillan Company. 1903. Price, $1.60.

The author states in the preface that "this book is the result of two years' instruction in dyeing in the classroom and in the laboratory. It aims to be a systematic presentation of the principles underlying the art of dyeing and emphasized by laboratory exercises. It attempts to apply to the teaching of dyeing the same methods of classroom work, which have proved so successful in the teaching of inorganic chemistry and other branches of the science."

The plan of study, which is followed, is to take two members of the first group of dyes and study these with special reference to their action toward the different fibers. Members of the second group of dyes are then taken up, and so on till all the groups have been considered.

A clear idea of the relations between the groups of dyes, their general properties, and their behavior towards different fibers having been gained in this way, the study of the groups of textile fibers is then taken up.

Following this comes the consideration of the machinery for dyeing and bleaching, and the methods of preparing the fibers or fabrics for the dyeing proper. Finally, the different groups of dyes are studied with the principles involved in their application to the different classes of material.

The book contains seventy-nine experiments to be performed by the student in the laboratory, these experiments being, so far as practicable, the processes used in dye-house work.

It is particularly unfortunate that the theories of dyeing given by the author on pages 51 and 52, are stated so briefly and also incorrectly. This part of the book should certainly be rewritten.

The book is well printed and bound and is provided with an excellent index. It can be most heartily recommended as a text-book to those desiring to teach or study the principles of dyeing. W. R. O.

INTRODUCTION TO THE RARER ELEMENTS. By PHILIP E. BROWNING, PH.D., Assistant Professor of Chemistry, Kent Chemical Laboratory, Yale University. New York: John Wiley & Sons; London: Chapman & Hall, Limited. 1903. 8vo. pp. viii + 157. Cloth, $1.50, net.

According to the preface, "This small volume, prepared from material used by the author in a short lecture-course given at Yale University, is intended to serve as a convenient handbook in the introductory study of the rarer elements; that is, of those elements which are not always taken up in a general cause in chemistry."

Advanced students ought certainly to pay more attention to these "rarer elements" than they commonly do, and this book will help them. The time required for a course like that laid out would be well spent. The book is clearly written and the directions for laboratory work are to the point.

The chapter devoted to gold is especially interesting. It is stated here that "As far back as 3600 B. C. in the Egyptian code of Menes, a ratio of value between gold and silver (2.5 : 1) is mentioned." Apparently they did more for silver in those days than the silver-tongued orator of the Chicago convention has since then hoped for and insisted upon.

The last chapter of the book treats of the newly discovered gases of the atmosphere and "recent unconfirmed discoveries." Even victorium, polonium, radium, and carolinium find mention here. I. R.

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$C_8H_7O_4N_2$. Methyl *m*-nitrobenzoate. *Stieglitz* and *Earle* 407
$C_8H_8O_3N_2$. Methyl imido-*m*-nitrobenzoate. *Stieglitz* and *Earle* 405
$C_8H_8O_3N_2$. *m*-Nitrobenzmethylamide. *Stieglitz* and *Earle* 408
$C_8H_{18}O_4S$. Diisobutyl sulphate. *Bushong* 222

4 VIII.

$C_8H_6O_3NBr_3$. Tribromnitrophenetol. *Jackson* and *Fiske* 71
$C_8H_7O_3NS$. Methyl ester of benzoic sulphinide. *Remsen* and *Clark* 278
$C_8H_7O_3NBr_3$. Dibromnitrophenetol. *Jackson* and *Fiske* 63
$C_8H_7O_3N_2Cl$. *N*-Methyl-*m*-benzchloramide. *Stieglitz* and *Earle* 408
$C_8H_7O_3N_2Cl$. Methyl chlorimido-*m*-nitrobenzoate. *Stieglitz* and *Earle* 403
$C_8H_7O_3N_2Cl$. *m*-Nitrobenzmethylchloramine. *Stieglitz* and *Earle* 404
$C_8H_7O_4NBr_2$. Dimethoxydibromnitrobenzol. *Jackson* and *Fiske* 70
$C_8H_7O_5SNa$. Sodium orthosulphonate of methyl benzoate. *Remsen* and *Bird* .. 270
$C_8H_7O_5SAg$. Silver orthosulphonate of methyl benzoate. *Remsen* and *Bird*. . 270
$C_8H_7O_7NS$. Acid methyl ester of *p*-nitro-*o*-sulphobenzoic acid. *Chambers* 387
$C_8H_9ONBr_2$. Dibromaminophenetol (dibromphenetidine). *Jackson* and *Fiske*. 66
$C_8H_9O_4NS$. *o*-Methylsulphaminebenzoic acid. *Remsen* and *Clark* 280
$C_8H_{11}O_2NS$. *o*-Toluenesulphone methylamide. *Remsen* and *Clark* 281
$C_8H_{11}O_5NS$. Methylammonium *o*-sulphobenzoate. *Remsen* and *Clark* 279

5 VIII.

$C_8H_6O_6NSCl$. *p*-Nitro-*o*-sulphone chloride of methyl benzoate. *Chambers*..... 387
$C_8H_6O_7NSNa$. Sodium methyl *p*-nitro-*o*-sulphobenzoate. *Chambers* 388
$C_8H_6O_7NSK$. Potassium methyl *p*-nitro-*o*-sulphobenzoate. *Chambers*.......... 388
$C_8H_7O_4NSK_2$. Potassium *o*-methylsulphaminebenzoate. *Remsen* and *Clark* .. 281

C_9-GROUP.

$C_9H_{10}O_3N_2$. β,δ-Dicyano-α-ketoglutaric ester. *Michael* 162
$C_9H_{11}O_2N$. Phenylurethane. *Wheeler* and *Johnson*.......................... 35
$C_9H_{11}O_3N$. Tyrosine in cheese. *Van Slyke* and *Hart*.......................... 7
$C_9H_{11}N_3S_2$. α-Phenyl-1-thiolmethylpseudodithiobiuret. *Johnson* and *Bristol* .. 172
$C_9H_{11}N_3S_2$. α-Phenyl-2-thiolmethylpseudodithiobiuret. *Johnson* and *Bristol*... 172
$C_9H_{12}N_2S$. *o*-Tolylthiolmethylpseudothiourea. *Johnson* and *Cramer*...... 179
$C_9H_{12}N_2S$. *p*-Tolylmethylpseudothiourea. *Johnson* and *Bristol*.. 173

4 IX.

$C_9H_9O_3NS$. Ethyl benzoic sulphinide. *Remsen* and *Clark*...................... 285
$C_9H_9O_5SNa$. Sodium *o*-sulphonate of ethyl benzoate. *Remsen* and *Bird* 269
$C_9H_{10}ON_2S_2$. Thiolmethyl ester of phenylthioallophanic acid. *Johnson* and *Elmer* 176
$C_9H_{11}O_4NS$. *o*-Ethylsulphaminebenzoic acid. *Remsen* and *Clark* 286
$C_9H_{12}O_3N_2S$. Dimethylamide of *o*-sulphobenzoic acid. *Remsen* and *Clark*..... 283
$C_9H_{13}O_5NS$. Ethylammonium sulphobenzoate. *Remsen* and *Clark* 287

5 IX.

$C_9H_8O_6NSCl$. *p*-Nitro-*o*-sulphone chloride of ethyl benzoate. *Chambers*........ 389
$C_9H_8O_7NSK$. Potassium ethyl *p*-nitro-*o*-sulphobenzoate. *Chambers*............ 390
$C_9H_9O_4NSK_2$. *o*-Ethylsulphaminebenzoate of potassium. *Remsen* and *Clark*. 286
$C_9H_{10}O_2N_2$. Acetylphenylurea. *Stieglitz* and *Earle* 418

C_{10}-GROUP.

$C_{10}H_9O_3N_3$. Acetylphenylurazole. *Wheeler* and *Johnson* 38
$C_{10}H_{13}N_3S_2$. α-Phenyl-2-thiolethylpseudodithiobiuret. *Johnson* and *Bristol* 173
$C_{10}H_{14}N_2S$. α,*p*-Tolyl-α-methylthiolmethylpseudothiourea. *Johnson* and *Bristol* 175
$C_{10}H_{22}O_4S$. Diisoamyl sulphate. *Bushong*.................................... 221

4 X.

$C_{10}H_{11}O_7NS$. Monopropyl ester of *p*-nitro-*o*-sulphobenzoic acid. *Chambers*.... 390
$C_{10}H_{12}ON_2S_2$. Thiolethyl ester of phenylthioallophanic acid. *Johnson* and *Cramer*... 181

5 X.

$C_{10}H_{10}O_6NSCl$. *p*-Nitro-*o*-sulphone chloride of propyl benzoate. *Chambers*.... 390
$C_{10}H_{10}O_7NSK$. Potassium propyl *p*-nitro-*o*-sulphobenzoate. *Chambers*........ 391

C_{11}-GROUP.

$C_{11}H_{16}O_3N_2S$. Diethylamide of *o*-sulphobenzoic acid. *Remsen* and *Clark*....... 287
$C_{11}H_{16}O_3N_2S$. Tetramethyldiamide of *o*-sulphobenzoic acid. *Remsen* and *Clark* 288

C_{12}-GROUP.

$C_{12}O_4Br_6$. Hexabromorthoquinopyrocatechin ether. *Jackson* and *Porter*....... 523

3 XII.

$C_{12}H_2O_4Br_6$. Hexabromorthodioxypyrocatechin ether. *Jackson* and *Porter* 525
$C_{12}H_{11}O_4N_3$. Diacetylphenylurazole. *Wheeler* and *Johnson* 37
$C_{12}H_{12}O_6N_2$. β,γ-Dicyano-α,δ-diketoadipic ethyl ester. *Michael* 160
$C_{12}H_{16}O_2N_3$. 1-Phenyl-3,5-diethylurazole. *Wheeler* and *Johnson* 38

4 XII.

$C_{12}H_7O_2N_2Br_3$. Tribromnitrodiphenylamine. *Jackson* and *Fiske* 77

C_{13}-GROUP.

$C_{13}H_6Cl_6$. Tetrachlorbenzophenone chloride. *Norris* and *Twieg* 398
$C_{13}H_8Cl_4$. Dichlorbenzophenone chlorides. *Norris* and *Twieg* 395
$C_{13}H_8Br_4$. *p*-Dibromdiphenylmethylene bromide. *Goldthwaite* 451
$C_{13}H_9Br_3$. *p*-Dibromdiphenylmethyl bromide. *Goldthwaite* 449
$C_{13}H_{10}Br_2$. *p*-Dibromdiphenylmethane. *Goldthwaite* 448
Also the *o*,*p*- and *o*-compounds.
$C_{13}H_{12}N_2$. *p*-Amidobenzylideneaniline. *Alway* and *Walker* 110

3 XIII.

$C_{13}H_6OBr_2$. *p*-Dibrombenzhydrol. *Goldthwaite* 457
Also the *o*,*p*- and *o*-compounds.
$C_{13}H_8OCl_2$. Dichlorbenzophenones. *Norris* and *Twieg* 396
$C_{13}H_8OBr_2$. *p*-Dibrombenzophenone. *Goldthwaite* 451
Also the *o*,*p*- and *o*-compounds.
$C_{13}H_{11}ON$. Benzanilide. *Wheeler* and *Johnson* 34
$C_{13}H_{12}O_2N_2$. *p*-Nitrobenzylaniline. *Alway* and *Walker* 105
$C_{13}H_{13}N_3S$. Diphenylthiosemicarbazide. *Johnson* and *Bristol* 173
$C_{13}H_{17}O_4N$. Ethyl anilinomalonate. *Curtiss* 133

4 XIII.

$C_{13}H_8ONBr$. *p*-Bromphenyl indoxazene. *Goldthwaite* 454
$C_{13}H_9ONBr_2$. *p*-Dibrombenzophenone oxime. *Goldthwaite* 452
Also the *o*,*p*-compound.
$C_{13}H_9NClBr$. *p*-Brombenzanilideimide chloride. *Wheeler* and *Johnson* 34
$C_{13}H_9O_3NS$. Anil of *o*-sulphobenzoic acid. *Remsen* and *Holmes* 275
$C_{13}H_9O_4SCl$. Orthosulphone chloride of phenyl benzoate. *Remsen* and *Humphreys* 302
$C_{13}H_9O_7NS$. Monophenyl *p*-nitro-*o*-sulphobenzoate. *Chambers* 377
$C_{13}H_{10}ONBr$. *p*-Brombenzanilide. *Wheeler* and *Johnson* 34
$C_{13}H_{10}O_6N_2S$. Phenyl *p*-nitro-*o*-sulphaminebenzoate. *Chambers* 385
$C_{13}H_{11}O_4NS$. Phenyl *o*-carbaminebenzenesulphonate. *Remsen* and *Humphreys* 300
$C_{13}H_{11}O_4NS$. Phenyl *o*-sulphaminebenzoate. *Remsen* and *Humphreys* 294

5 XIII.

$C_{13}H_8O_3NSBr$. Anil of parabromorthosulphobenzoic acid. *Blanchard* 493
$C_{13}H_8O_6NSCl$. *p*-Nitro-*o*-sulphone chloride of phenyl benzoate. *Chambers* 376
$C_{13}H_8O_7NSK$. Potassium phenyl *p*-nitro-*o*-sulphobenzoate. *Chambers* 378

C_{14}-GROUP.

$C_{14}H_{12}O_2N_2$. Benzoylphenylurea. *Stieglitz* and *Earle* 418
$C_{14}H_{18}O_5N_2$. Ethyl nitrosoorthotoluidinomalonate. *Curtiss* 137
Also the meta- and para-compounds.

$C_{14}H_{19}O_4N$. Ethyl orthotoluidinomalonate. *Curtiss*.......... 135
Also the hydrochloride and the corresponding meta- and para-compounds.

4 XIV.

$C_{14}H_{10}O_2NCl$. Dibenzoylchloramine (dibenzoylchlorimide). *Stieglitz* and *Earle*.......... 420
$C_{14}H_{10}O_3N_2Br_4$. Methoxydibromazoxybenzol. *Jackson* and *Fiske*.......... 60
$C_{14}H_{11}O_2N_2Cl$. Benzoyl-*p*-chlorphenylurea. *Stieglitz* and *Earle*.......... 416
$C_{14}H_{11}O_4SCl$. Orthosulphone chloride of *o*-cresyl benzoate. *Remsen* and *Humphreys*.......... 309
$C_{14}H_{12}ONCl$. Anisanilideimide chloride. *Wheeler* and *Johnson*.......... 37
$C_{14}H_{13}O_4NS$. Cresyl *o*-sulphaminebenzoate. *Remsen* and *Humphreys*.......... 299

5 XIV.

$C_{14}H_{10}O_6NSCl$. *p*-Nitro-*o*-sulphone chloride of *o*-cresyl benzoate. *Chambers*.......... 379
Also the *p*-cresyl compound.

C_{15}-GROUP.

$C_{15}H_{12}O_2Br_2$. *p*-Dibrombenzhydrol acetate. *Goldthwaite*.......... 456
Also the *o,p*- and *o*-compounds.
$C_{15}H_{13}O_2N$. Acetbenzanilide. *Wheeler* and *Johnson*.......... 35
$C_{15}H_{14}OBr_2$. *p*-Dibrombenzhydrol ethyl ether. *Goldthwaite*.......... 461
$C_{15}H_{15}N_3S_2$. *a,c*-Diphenyl-1-thiolmethylpseudodithiobiuret. *Johnson* and *Elmer*.......... 176

C_{16}-GROUP.

$C_{16}H_{15}O_3N$. Benzoylphenylurethane. *Wheeler* and *Johnson*.......... 35
$C_{16}H_{17}N_3S_2$. *a,c*-Diphenyl-*a*-methyl-1-thiolmethylpseudodithiobiuret. *Johnson* and *Elmer*.......... 177
$C_{16}H_{17}N_3S_2$. *a,c*-Diphenyl-1-thiolethylpseudodithiobiuret. *Johnson* and *Cramer* 181
$C_{16}H_{17}N_3S_2$. *a*-Phenyl-*c*-orthotolyl-1-thiolmethylpseudodithiobiuret. *Johnson* and *Cramer*.......... 180
$C_{16}H_{17}N_3S_2$. *a,o*-Tolyl-*c*-phenyl-1-thiolmethylpseudodithiobiuret. *Johnson* and *Cramer*.......... 179
$C_{16}H_{17}N_3S_2$. *a,p*-Tolyl-*c*-phenyl-1-thiolmethylpseudodithiobiuret. *Johnson* and *Bristol*.......... 174

4 XVI.

$C_{16}H_{14}O_3N_2Br_4$. Ethoxydibromazoxybenzol. *Johnson* and *Fiske*.......... 65
$C_{16}H_{14}O_{10}S_2Ba$. Barium orthosulphonate of methyl benzoate. *Remsen* and *Bird* 270
$C_{16}H_{18}N_3S_2I$. *a,c*-Diphenyl-1,2-thiolmethyldipseudodithiobiuret. *Johnson* and *Elmer*.......... 177

C_{17}-GROUP.

$C_{17}H_{19}N_3S_2$. *a,c*-Diorthotolyl-1-thiolmethylpseudodithiobiuret. *Johnson* and *Cramer*.......... 182
$C_{17}H_{19}N_3S_2$. *a*-Phenyl-*c*-orthotolyl-1-thiolethylpseudodithiobiuret. *Johnson* and *Cramer*.......... 181
$C_{17}H_{19}N_3S_2$. *a,p*-Tolyl-*a*-methyl-*c*-phenyl-1-thiolmethylpseudodithiobiuret. *Johnson* and *Bristol*.......... 175
$C_{17}H_{19}N_3S_2$. *a,o*-Tolyl-*c*-phenyl-1-thiolethylpseudodithiobiuret. *Johnson* and *Cramer*.......... 180

$C_{17}H_{19}N_3S_2$. a,*o*-Tolyl-*c*-phenyl-1,2-thiolmethyldipseudodithiobiuret. *Johnson* and *Cramer*.......... 179
$C_{17}H_{19}N_3S_2$. a,*p*-Tolyl-*c*-phenyl-1,2-thiolmethyldipseudodithiobiuret. *Johnson* and *Bristol*.......... 174

C_{18}-GROUP.

$C_{18}H_{21}N_3S_2$. a,*c*-Diorthotolyl-1-thiolethylpseudodithiobiuret. *Johnson* and *Cramer*.......... 181

4 XVIII.

$C_{18}H_{12}O_2N_2Br_2$. Dianilinodibromorthobenzoquinone. *Jackson* and *Porter*...... 526

5 XVIII.

$C_{18}H_{16}O_{14}N_2S_2Ba$. Barium ethyl *p*-nitro-*o*-sulphobenzoate. *Chambers*.......... 389

C_{19}-GROUP.

$C_{19}H_{14}Br_2$. *p*-Dibromtriphenylmethane. *Goldthwaite*.......... 463

3 XIX.

$C_{19}H_6O_5Br_6$. Monobenzoyl derivative of hexabromorthodioxypyrocatechin ether. *Jackson* and *Porter*.......... 525
$C_{19}H_{14}O_5S$. Diphenyl ester of *o*-sulphobenzoic acid. *Remsen* and *Humphreys*. 294

4 XIX.

$C_{19}H_{11}O_{11}N_3S$. Dinitrophenyl ester of *p*-nitro-*o*-sulphobenzoic acid. *Chambers* 382
$C_{19}H_{13}O_7NS$. Diphenyl *p*-nitro-*o*-sulphobenzoate. *Chambers*.......... 394
$C_{19}H_{16}O_3N_2S$. Anilides of *o*-sulphobenzoic acid. *Remsen* and *Holmes*.......... 275
$C_{19}H_{16}O_3N_2Br_2$. Addition-compound of methyl alcohol and dianilinodibromorthobenzoquinone. *Jackson* and *Porter*.......... 531

5 XIX.

$C_{19}H_{13}O_2N_2SBr$. Dianil of parabromorthosulphobenzoic acid. *Blanchard*..... 497
$C_{19}H_{15}O_3N_2SBr$. Anilides of parabromorthosulphobenzoic acid. *Blanchard*... 491

C_{20}-GROUP.

$C_{20}H_9N_2Br_3$. Diphenylenetribromquinoxaline. *Jackson* and *Fiske*.......... 79
$C_{20}H_{11}N_2Br_3$. Diphenyltribromquinoxaline. *Jackson* and *Fiske*.......... 79
$C_{20}H_{14}O_4N_2$. *m*-Nitrobenzoylbenzanilide. *Wheeler* and *Johnson*.......... 37
$C_{20}H_{17}O_4N_3$. *bis-p*-Nitrobenzylaniline. *Alway* and *Walker*.......... 108

4 XX.

$C_{20}H_{14}O_2NBr$. *p*-Brombenzoylbenzanilide. *Wheeler* and *Johnson*.......... 33
$C_{20}H_{18}O_3N_2Br_3$. Addition-compound of ethyl alcohol and dianilinodibromorthobenzoquinone. *Jackson* and *Porter*.......... 529

5 XX.

$C_{20}H_{20}O_{14}N_2S_2Ba$. Barium propyl *p*-nitro-*o*-sulphobenzoate. *Chambers*........ 391

C_{21}-GROUP.

$C_{21}H_{17}O_3N$. Benzoylanisanilide. *Wheeler* and *Johnson*.......... 36

$C_{21}H_{19}N_3S_2$. α,ε-Diphenyl-1-thiolbenzylpseudodithiobiuret. *Jackson* and *Bristol* 177

4 XXI.

$C_{21}H_{17}O_7NS$. Di-*o*-cresyl ester of *p*-nitro-*o*-sulphobenzoic acid. *Chambers* 379
Also the *p*-cresyl ester.

C_{22}-GROUP.

$C_{22}H_{17}N_3S_2$. Triazine (?) made from phenylthiolbenzylpseudothiourea and benzoyl isothiocyanate. *Johnson* and *Elmer* 178
$C_{22}H_{19}O_3N$. Oxyphenylethylamine in cheese. *Van Slyke* and *Hart* 8

C_{24}-GROUP.

$C_{24}H_{19}ON_3$. Dianilinoparaquinoneanil. *Jackson* and *Porter* 534

4 XXVI.

$C_{24}H_{18}ON_3Br$. Dianilinobromparaquinoneanil. *Jackson* and *Porter*. 531
$C_{24}H_{19}O_2N_3Br_2$. Addition-compound of aniline and dianilinodibromorthobenzoquinone. *Jackson* and *Porter* 527

C_{26}-GROUP.

$C_{26}H_{16}Br_4$. *p*-Tetrabromtetraphenylethylene. *Goldthwaite* 455
$C_{26}H_{18}Br_4$. *p*-Tetrabromtetraphenylethane. *Goldthwaite* 458

3 XXVI.

$C_{26}H_{18}OBr_4$. *p*-Dibrombenzhydrol ether. *Goldthwaite* 460
$C_{26}H_{20}ON_2$. Benzoylbenzenyldiphenylamidine. *Wheeler* and *Johnson* 36
$C_{26}H_{22}ON_4$. *p*-Azoxybenzylideneaniline. *Alway* and *Walker* 109

5 XXVI.

$C_{26}H_{16}O_{14}N_2S_2Ba$. Barium phenyl *p*-nitro-*o*-sulphobenzoate. *Chambers* 378

C_{27}-GROUP.

$C_{27}H_{17}O_7NS$. β-Naphthyl ester of *p*-nitro-*o*-sulphobenzoic acid. *Chambers* ... 384

C_{36}-GROUP.

$C_{36}H_{28}O_4N_4Br_2$. Substance formed by the reduction of dianilinodibromorthoquinone. *Jackson* and *Porter* 535

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